VOL. II. [JUNE, 1880.] No. 2.

AMERICAN CHEMICAL JOURNAL.

ON THE DETERMINATION OF ALBUMINOIDS IN HAY AND COARSE FODDERS.

BY H. P. ARMSBY.

In the analysis of feeding-stuffs and of vegetable products in general, the albuminoids are commonly determined by multiplying the percentage of nitrogen found by analysis by 6.25, it being assumed that the albuminoids contain 16 per cent. of nitrogen, and that no other nitrogenous bodies are present. Recent investigations have, however, shown that the latter assumption in particular is frequently far from being true, and that many feeding-stuffs contain relatively large amounts of non-albuminoid nitrogenous matters, consisting chiefly of amides. These bodies have been found to be especially abundant in beets and other roots, in potatoes, and in grass and hay, while the seeds of plants appear to be comparatively free from them.

In view of the probable inferior nutritive value of these amides and other bodies, which we shall here designate for convenience as *non-albuminoids*, it becomes desirable, in the analysis of a feeding-stuff, to be able to separate them from the albuminoids and to determine their amount. Much the same difficulties which stand in the way of a direct determination of the albuminoids prevent a direct determination of the non-albuminoids as well; but, on the other hand, a more or less perfect separation of the albuminoid and

non-albuminoid *nitrogen* may be made without special difficulty. Several processes have been proposed to effect this, all of which assume as their starting point that the non-albuminoids are soluble in water or acid liquids. Now, while this is true of all the bodies of this class known to exist in feeding-stuffs, and while it is very probably correct, it should be borne in mind that it is not proved. There is no reason in the nature of things why there should not be an insoluble amide, for example, as well as an insoluble albuminoid. If there be such, however, we have no means of ascertaining the fact at present, and can only adopt provisionally the assumption just mentioned as a working hypothesis.

Taking this as a starting point, the several methods proceed in general as follows:

The substance to be examined is first boiled with water slightly acidified with some organic acid or with water alone; this process dissolves out the non-albuminoids (with the reservation made above), while most or all of the albuminoids are either not dissolved at all or are coagulated by boiling. Some substance is then added to the liquid which will precipitate any dissolved albuminoids which it may still contain, without affecting the non-albuminoids, the mass is filtered, and a nitrogen determination made either in the insoluble matters or in the filtrate.

In the first case we get directly the albuminoid nitrogen, in the second case it is obtained by subtracting the nitrogen of the filtrate from the total nitrogen of the substance. The several methods differ essentially only in the precipitant employed. Church* recommends a four per cent. solution of carbolic acid, Sestini† uses lead acetate, Dehmel‡ has obtained concordant results by the use of copper sulphate as proposed by Ritthausen, and E. Schulze§ proposes the use of ferric acetate as recommended by Hoppe-Seyler. More or less uncertainty, however, is involved in all these methods, since, although the precipitants employed doubtless remove all the albuminoids from solution, we are largely ignorant of the nature of the amides and other bodies extracted by water, and run the risk of precipitating them from the solution by means of the reagents intended to effect the removal of albuminoids.

These considerations led the writer to experiment on the possibility of dispensing with precipitants altogether, and the results on

* Laboratory Guide, 4th ed., 209.
† Landw. Versuchs-Stationen, 23, 305.
‡ Ibid. 24, 214.
§ Landw. Jahrbücher, 6, 160.

hay have been so satisfactory that he feels induced to describe the method adopted.

Comparative trials were first made on three samples of hay which had previously been analyzed, carbolic acid, lead acetate, and cupric sulphate being all used as precipitants.

The experiments with carbolic acid and lead acetate were made according to the directions of Church and Sestini respectively. In the experiments with cupric sulphate the substance was boiled for an hour with water, then 10 c. c. of a ten per cent. solution of cupric sulphate was added, the boiling continued for a few minutes, the mass then filtered, and the nitrogen of the insoluble residue determined.

In the trials with water the substance was simply boiled for an hour with water slightly acidified with lactic acid, filtered, and treated as in the other methods. In each trial 0.5 gram of hay was used, and each result is the mean of two accordant determinations.

	No. 1.	No. 2.	No. 3.
Water,	11.31 per cent.	10.75 per cent.	11.19 per cent.
Total nitrogen,	1.30 "	0.81 "	2.39 "
Albuminoid nitrogen,			
By Church's method,	1.22 "	0.68 "	1.93 "
By Sestini's "	1.18 "	0.62 "	1.83 "
By copper sulphate method,	1.22 "	0.69 "	1.89 "
By extraction with water,	1.11 "	0.61 "	1.92 "
Average,	1.18 "	0.65 "	1.89 "
Non-Albuminoid nitrogen,	0.12 "	0.16 "	0.50 "

In all cases (except in Church's method, where it is impossible)* the filtrate was tested for albuminoids by Millon's reagent and found to be free from them.

These results show: first, that these samples of hay contained a considerable proportion of non-albuminoid nitrogen; second, that all four of the methods used for the determination of albuminoid nitrogen gave practically the same result, and consequently the use of any reagent to precipitate dissolved albuminoids was unnecessary in these cases.

In addition to these experiments, the albuminoid nitrogen in

* In endeavoring to test the filtrate obtained by Church's method it was found that carbolic acid gives with Millon's reagent a color which, in very dilute solutions, simulates closely that produced by albuminoids, except that it appears, after a time, in the cold. This fact does not appear to have been previously noticed.

twenty-one samples of hay and stover has been determined by treatment with water in the manner described above, and in no case could albuminoids be detected in the filtrate, so that we are justified in concluding that in the analysis of hay a separation of the albuminoid and non-albuminoid nitrogen may be effected most simply by means of boiling water. That this method is preferable to the use of precipitants is obvious. Whether it is applicable to all feeding-stuffs is perhaps doubtful. Some experiments on rye-bran and malt sprouts seem to indicate that it is not, but to hay at least it is perfectly applicable, and by its aid it is a very simple matter to determine the amount of albuminoid nitrogen present, and by multiplication by 6¼ to calculate approximately the amount of albuminoids.

To ascertain whether the method of extraction adopted brought all the non-albuminoids into solution, the following trials were made on a sample of clover hay containing 2.41 per cent. of nitrogen. One-half gram of the hay was boiled with slightly acidulated water for 45 minutes, filtered through an asbestos filter, and the insoluble residue burned with soda-lime. A second portion of one-half gram was boiled with acidulated water for 30 minutes, filtered through asbestos, the residue returned to the dish, boiled 30 minutes longer with acidulated water, and then filtered and burned as before. A third portion was submitted to three extractions in the same manner. Each experiment was made in duplicate, and the following results obtained for albuminoid nitrogen:

One extraction,	1.85	and 1.89	per cent.
Two extractions,	1.78	1.87	"
Three extractions,	1.82	1.84	"

Evidently one extraction removed all the soluble nitrogen.

A diffusion experiment was also made, to see if there were any indications of the presence of soluble albuminoids in the filtrate. Twenty grams of the hay were boiled for forty-five minutes with acidulated water, filtered, and washed with hot water. The filtrate was introduced into a parchment paper dialyser and allowed to diffuse into a constantly renewed volume of water for nearly two days. It was then diluted to 1000 c. c., and two portions of 50 c. c. evaporated to dryness in Hofmeister glass capsules and burned with soda lime. Calculated on the original substance, the results were 0.08 per cent. and 0.10 per cent. of nitrogen, or an average of 0.09

per cent., as the amount of indiffusible nitrogen extracted by this process.

It would thus appear that the method of extraction with boiling water effects a very satisfactory separation of the albuminoid and non-albuminoid nitrogen of hay. It has the advantage of simplicity, and while its results are, like all the results of fodder analysis, sufficiently crude, they are no more so than those obtained by the use of more complicated methods, and are an advance on those reached by simply determining the total nitrogen.

CONNECTICUT AGRICULTURAL EXPERIMENT STATION, March, 1880.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.

No. III.

PARACHLORBENZYL COMPOUNDS.*

BY C. LORING JACKSON AND ALFRED W. FIELD.

Parachlorbenzylchloride, $C_6H_4ClCH_2Cl$. In beginning these researches, we had no idea that it would be necessary to investigate this substance, as, since its discovery by Beilstein and Geitner,† it had been prepared and studied by a great number of chemists, and had served as the starting-point for the preparation of all the parachlorbenzyl compounds known. But, on looking into the subject more carefully, we found that it had been made invariably from the product of the chloriring of toluol in the cold, which Hübner and Majert‡ have proved, by their work on the sulphoacids, is a mixture of ortho- and parachlortoluol; while, more recently, Oscar Emmerling§ has shown that the product from ox-

* Proceedings American Academy of Arts and Sciences. Communicated by the Authors.

† Beilstein and Geitner, Zeitschr. der Chem. 1866, 307; also 17.

‡ Hübner and Majert, Ber. d. ch. G. 6, 790.

§ O. Emmerling, Ber. d. ch. G. 8, 880.

idizing it with potassic permanganate contains more ortho- than parachlorbenzoic acid. The parachlorbenzylchloride of previous chemists, therefore, must have been contaminated with a larger or smaller amount of the ortho compound, which escaped detection, because the method used by them to test the purity of their preparations consisted in oxidizing with potassic dichromate and sulphuric acid, and, as this destroys the ortho modification completely, a pure parachlorbenzoic acid was the only product. This oversight is not surprising when it is borne in mind that the more important of these papers appeared in 1866, when the nature of aromatic isomeres was very imperfectly understood.

For the reason given above, we determined to prepare the parachlorbenzylchloride from perfectly pure parachlortoluol, and hoped that it might be a solid, instead of the oily liquid described by our predecessors; indeed, it seemed hard to believe that it could be a liquid, as the parachlortoluol melts at 6½° (Hübner and Majert), and we have found that the introduction of bromine into the side-chain raised the melting-point to 48½°.

Preparation. Parachlortoluol was made from pure paratoluidine by treatment with hydrochloric acid and potassic nitrite, according to a modification of the method of Hübner and Majert* described in connection with parachlorbenzylbromide in the first paper† of this series. The 31 grams that we obtained distilled over completely between 160° and 161°, and froze between 4° and 5° in white plates looking exactly like parabromtoluol, which melted from 7° to 7½°. These results agree essentially with those of Hübner and Majert,* who found the boiling-point 160½°, the freezing-point a little above 0°, and the melting-point 6½°. To convert this into parachlorbenzylchloride, a stream of chlorine was passed into it while it stood in a paraffine-bath heated to 166°: when the increase in weight showed that somewhat more than the calculated amount of chlorine had been taken up (the 27 grams of parachlortoluol used had become 35 grams instead of 34.3 grams,) the chlorine was stopped, and the product put in a freezing mixture of ice and salt, where it partially solidified in white needles, which were drained on the filter-pump, and recrystallized from alcohol. The yield was very small, and all attempts to get more from the mother-liquors were fruitless. The following analyses of the substance dried *in vacuo* show that it is the expected parachlorbenzylchloride.

* Hübner and Majert, Ber. d. ch. G. 6, 794. † This Journal, I, 100.

0.6760 gram of substance gave 1.2930 gram of CO_2 and 0.2458 gram of H_2O.*

0.2755 of substance gave, by Klobukowski's† modification of Emil Kopp's method, 0.4946 gram AgCl.

	Calculated for $C_7H_6Cl_2$.	Found.
Carbon,	52.17	52.17
Hydrogen,	3.73	4.04
Chlorine,	44.10	44.41
	100.00	100.62

Properties. White lustrous prisms or needles, often more than 3 cm. long, with an agreeable aromatic odor and most violent action on the mucous membrane and tenderer parts of the skin; melting point, 29°; so volatile that a crystal exposed to the air disappears in a few hours; sublimes even at ordinary temperatures in needles; it is very little, if at all, soluble in water, but readily in warm, less so in cold, alcohol, very easily in ether, benzol, carbonic disulphide, and glacial acetic acid. That it is a chlorbenzyl compound was proved by boiling it for some time with water, in a flask with a return-cooler, when the parachlorbenzylalcohol and hydrochloric acid were formed. Boiled with a solution of potassic permanganate, it was easily oxidized, giving an acid which melts between 233° and 235° (O. Emmerling gives 234° as the melting-point of parachlorbenzoic acid); this acid boiled with water, in which the orthochlorbenzoic acid is much more soluble than the para, gave a solution which deposited crystals melting also at 233°–235°: as potassic permanganate oxidizes instead of destroying the ortho compounds, this proves that our parachlorbenzylchloride is perfectly free from isomeric impurities.

Having thus proved that the parachlorbenzylchloride used as a starting point for the preparation of derivatives by Beilstein, Kuhlberg, Neuhof, and others, really did contain the ortho compound, as we had previously inferred, we next proceeded to make some of these derivatives, and redetermine their properties. In this work, the more easily purified parachlorbenzylbromide was used instead of the chloride.

*Combustion of these parachlorbenzyl compounds with plumbic chromate alone was found to yield good results much more easily than the more usual method of combustion in a stream of oxygen, and therefore was used in the analysis of all these substances.

†Klobukowski, Ber. dt. ch. G. 10, 290.

Parachlorbenzylalcohol, $C_6H_4ClCH_2OH$, was made by boiling the bromide (or chloride) with water in a flask with a return-cooler. The formation of hydrobromic (or hydrochloric) acid by this reaction was proved by testing the water, which had become acid, with argentic oxide, when argentic bromide (or chloride) was formed, and the acid reaction disappeared. The alcohol was made also from the acetate by boiling with water; sealing with aqueous ammonia, as recommended by Beilstein and Kuhlberg, being found in this case unnecessary; it was purified by crystallization from boiling water, dried *in vacuo*, and analyzed.

0.4517 gram of substance gave 0.9754 gram CO_2 and 0.2175 gram H_2O.

	Calculated for C_7H_6ClOH.	Found.
Carbon	58.94	58.89
Hydrogen	4.91	5.34

Properties. Beautiful pointed white ribbons usually one or two inches long, with a brilliant pearly lustre and characteristic smell, but no action on the mucous membrane or tenderer parts of the skin; melting point, 70½°; sublimes very easily in white needles, and can be purified in this way; evaporates slowly on exposure to the air, and distils in a current of steam; slightly soluble in cold, much more so in hot water, very easily in alcohol, ether, benzol, carbonic disulphide, and glacial acetic acid. It is oxidized by a mixture of potassic dichromate and dilute sulphuric acid, giving parachlorbenzoic acid; melting-point, 233° (234° O. Emmerling.)

The chlorbenzylalcohol obtained by Beilstein and Kuhlberg* differs from the above only in melting at 66°.

Parachlorbenzylcyanide. The product of the reaction of alcoholic parachlorbenzylbromide and potassic cyanide, when precipitated by water, was a yellow oil, which showed no signs of solidifying in a mixture of ice and salt: after standing in an open watch-glass for three or more weeks, however, it did deposit crystals when put in a freezing-mixture, but in such small quantity that it was impossible to purify them thoroughly; and it did not seem worth while to spend the large amount of time and material necessary to get enough of them for complete study. The crystals, after sucking out the oil with filter-paper, proved to be good-sized colorless prisms; and, as one specimen of a twinned form like a quatrefoil was observed, there can be no doubt that the substance is analogous to the parabrom-

* Beilstein and Kuhlberg, Ann. Chem. Pharm. 147, 339.

benzylcyanide, which will be described in a later paper of this series; its melting-point is 29°; and it is easily soluble in alcohol and ether, being left on evaporation of the solvent as an oil which crystallizes when stirred.

The yellow oil from which the crystals were obtained has also the nitrile smell, and is converted by heating to 100° in a sealed tube with hydrochloric acid, into parachloralphatoluylic acid: it must therefore be either the same substance as the crystals, prevented from solidifying by a small quantity of impurity, or the crystals may be a polymeric form of the oil. The cyanide was mentioned by Neuhof* as a dark oil, made by heating chlorbenzylchloride to 120°–130° in a sealed tube with potassic cyanide and alcohol; but no attempt was made to purify or analyze it. This heating in a sealed tube to 120°–130° is, as seen from the above, unnecessary.

Parachloralphatoluylic Acid, $C_6H_4ClCH_2COOH$, made by heating the nitrile to 100° in a sealed tube with fuming hydrochloric acid, or by boiling it with dilute sulphuric acid in a flask with a return-cooler, was purified by solution in ammonic hydrate, precipitation with sulphuric acid, and recrystallizing from boiling water. Its composition was established by an analysis of the silver salt.

Properties. White needles, often two centimetres long, sometimes thick and pointed, with a pleasant smell; melting-point, 103½°–104°; sublimes easily in little plates, and can be distilled, although not quickly, in a current of steam; somewhat soluble in cold, much more so in hot water, freely in alcohol, ether, benzol, carbonic disulphide, and glacial acetic acid. Aqueous ammonia dissolves it readily, but the ammonic salt is decomposed, at least in part, by evaporation, the acid being set free.

A chloralphatoluylic acid has been already described as the para compound by Neuhof,† who made it, however, from chlorbenzylchloride; the melting-point was 60°, and it separated from its salts as an oil which soon solidified, otherwise it resembled our acid, except that it seems to have been much more soluble in water. Later, Radziszewski‡ made a similar acid, melting at 68°, by chloriring alphatoluylic acid.

Argentic Parachloralphatoluylate, $C_6H_4ClCH_2COOAg$, fell as a white, curdy precipitate, upon adding argentic nitrate to a neutral solution of the ammonic salt of the acid. It was washed with water, dried at 100°, and analyzed.

* Neuhof, Ann. Chem. Pharm. 147, 347. † Ibid. 147, 347.
‡ Radziszewski, Ber. d. ch. G. 2, 207.

0.3410 gram of substance gave, precipitated from a nitric acid solution, with hydrochloric acid, 0.1788 gram of AgCl.

	Calculated for $C_6H_6ClO_2Ag$.	Found.
Silver	38.91	39.44

Properties. A white, curdy mass, consisting of clumps of silky microscopic needles, which blackens rapidly in direct sunlight, but only very slowly in diffused daylight, very slightly soluble in boiling water, almost insoluble in cold, freely soluble in dilute nitric acid and ammonic hydrate.

Neuhof obtained a similar salt, but describes it as more soluble in water than ours.

We did not succeed in getting a pure, well-defined *calcic salt*, although we tried to do so several times. By adding lime-water to the acid till the reaction was alkaline, removing the excess of lime by carbonic dioxide, and allowing the solution to evaporate spontaneously, arborescent groups of white needles were obtained. These lost 9.84 per cent. when dried at 100°; 2 molecules of crystal water would give 8.68 per cent.; 2½ molecules, 10.61 per cent.; the loss, therefore, does not correspond to any probable amount of water of crystallization, and it seemed likely that something beside water was given off, as there was a slight sublimate on the upper watch-glass, and the substance had become somewhat brown, with a semifused look very unlike its original appearance. It, however, contained 10.36 per cent. of calcium, and may therefore have been the anhydrous salt which needs 10.55 per cent. Other experiments under different conditions gave no better results, and we therefore decided that the salt was not important enough to repay a thorough study, which would use up a great deal of time.

The *baric salt* was even less well defined than the calcic; it was prepared in the same way, and appeared on evaporation of its solution over sulphuric acid as a colorless varnish, part of which changed on stirring into a radiated crystalline mass. This became white and opaque when treated with cold water, and when boiled with water gave an acid reaction and the smell of the acid. If the solution was evaporated on the water-bath instead of over sulphuric acid, a sticky gum was left. Neuhof's baric salt was similar to ours, and gave him an amount of barium corresponding to an acid salt. His calcic salt, on the other hand, contained one molecule of water, which it lost at 100°.

A solution of the acid in ammonic hydrate, from which the excess of ammonia has been driven off on the water-bath, gives the following characteristic reactions — bluish-green flocks with *cupric sulphate*, yellowish-brown with *ferric chloride*, and white with *plumbic acetate* or *mercurous nitrate*.

Parachlorbenzylsulphocyanate, $C_6H_4ClCH_2SCN$, made by boiling the bromide with an alcoholic solution of potassic sulphocyanate, was purified by freezing with snow and salt, sucking out the oil with filter paper, and recrystallization from alcohol with the help of a freezing mixture. It was dried *in vacuo* and analyzed.

0.1569 gram substance gave 0.1985 gram $BaSO_4$.

	Calculated for C_7H_6ClSCN.	Found.
Sulphur	17.43	17.38

Properties. White, flattened needles, often over an inch long, with a strong, disagreeable smell; melting-point, 17°; does not distil with steam, but seems to be slowly decomposed by it, a few brown drops with a smell like that of benzaldehyd passing over; mixes with alcohol, ether, benzol, carbonic disulphide, and glacial acetic acid, but not with water.

This substance has not been made heretofore: it resembles the corresponding bromine compound very closely in everything but melting-point.

Parachlorbenzylamines.

These substances have been studied already by Berlin,* who prepared them by heating the chlorbenzylchloride with alcoholic ammonia for one week in the steam-bath. The product was worked up by a needlessly complex process, consisting, when stripped of its unnecessary steps, in separating one portion of the bases by conversion into their chlorides and crystallizing from alcohol, while in the remainder the tertiary amine was destroyed by distillation with bromine and water, and the bromides of the remaining amines separated by crystallization. The properties of the tertiary and primary amines, as described by him, are in no way peculiar; but he obtained four isomeric forms of the secondary amine, which were themselves undistinguishable yellow oils, but differed in the melting-points of their salts, as shown in the following table:—

* Berlin, Ann. Chem. Pharm. 151, 137.

Name of Salt.	Melting Points.			
	α	*β*	*γ*	*δ*
Chloride	288°–289°	225°–228°	218°–220°	221°–222°
Bromide	283°–290°	224°	210°–212°	198°–199°
Iodide	. . . .	215°	187°	216°–218°
Nitrate	. . . .	204°–205°	193°	177°–179°

These salts also differed in solubility, the *α* modification being the least, the *δ* the most soluble: they were separated by crystallization of the bromides from water. These observations rendered a repetition of Berlin's work very interesting; but we did not follow the process given by him, as we have found a much more easy and simple method for the separation of the bases. Alcoholic ammonia acted very quickly, even in the cold, on parachlorbenzylbromide: the product from this or from the action in a sealed tube at 100° consisted of crystals either of the bromide of the tertiary amine or of the base itself, and of an alcoholic solution, which, filtered off and evaporated on the steam-bath, yielded the bromides of ammonium and of the primary and secondary amines with some free tertiary amine. This residue, after washing with water to remove the bromides of ammonium and the primary amine, was repeatedly crystallized from hot alcohol, until it was divided into slightly soluble scales of secondary bromide and needles of the free tertiary amine readily soluble in boiling alcohol.

Triparachlorbenzylamine, $(C_6H_4ClCH_2)_3N$, was freed from a trace of bromide by crystallizing from ether, dried *in vacuo*, and analyzed.

0.7096 gram of substance gave 1.6780 gram CO_2, and 0.3300 gram H_2O.

	Calculated for $(C_7H_6Cl)_3N$.	Found.
Carbon	64.78	64.49
Hydrogen	4.61	5.16

Properties. Bunches of white needles, when crystallized from alcohol; from ether it separates as an oil, which solidifies after some time in flattened prisms: it is also deposited from the action of cold alcoholic ammonia on parachlorbenzylbromide in short, thick, well-formed crystals, with rhombic faces; melting-point, 78½°; insoluble in water, very slightly soluble in cold, freely in hot alcohol, and in ether, benzol, and carbonic disulphide, less so in glacial acetic acid.

The *chloride* was obtained in an impure state when an alcoholic solution of the base was heated with strong hydrochloric acid; after standing 24 hours, the solution was allowed to evaporate spontaneously, when balls of radiated needles were left which melted at about 196°, were soluble in alcohol, ether, and glacial acetic acid, slightly in water, and insoluble, or nearly so, in carbonic disulphide and benzol; the alcoholic solution left a viscous mass, which changed into needles slowly. After drying *in vacuo*, it lost, in the steam-bath, an amount equal to less than one molecule of water; but its melting-point was unaltered, and, as it yielded crystals of the free amine on repeated treatment with alcohol, it does not follow that the loss was nothing but water. We could find no satisfactory method of purifying this, or of making a purer substance. The *bromide* obtained in the preparation of the amine crystallizes in scales like those of the bromide of the secondary amine soon to be described, but less soluble in alcohol.

Triparachlorbenzylamine Chlorplatinate, $[(C_6H_4ClCH_2)_3NH]_2PtCl_6$, was made by adding aqueous chlorplatinic acid to an ethereal solution of the base, and washing with water, alcohol and ether; dried at 100°, it gave the following results on analysis:

I. 0.2380 gram substance gave 0.0405 gram platinum.

II. 0.2796 gram substance gave 0.0471 gram platinum.

		Found.	
Calculated for $[(C_7H_6Cl)_3NH]_2PtCl_6$.	I.	II.
Platinum,	16.54	17.01	16.84

Properties. Pale orange microscopic irregular plates, almost insoluble in water, alcohol and ether.

It is worthy of especial note that Berlin's tertiary chlorbenzylamine melted at 88°–89°, as this is the only case in which we have found the melting-point of the pure substance lower than that of the impure. His chloride melting-point, 170°–175°, crystallized in well-formed rhombohedra with two molecules of water, which it lost *in vacuo*. Our (impure) salt differed from his not only in appearance and melting-point, but also in losing nothing *in vacuo*; and we have never observed any rhombohedra like those described by him, although we have tried very often and under various conditions to obtain them.

Diparachlorbenzylamine, $(C_6H_4ClCH_2)_2NH$. The bromide of this base, separated from the other amines as described above, and purified by repeated boiling with alcohol, was decomposed with

aqueous sodic hydrate; the oil thus obtained solidified on stirring, especially if it was touched with a crystal of the substance.

Properties. White radiating bladed crystals; melting-point, 29°; insoluble in water, soluble in alcohol and glacial acetic acid, freely soluble in ether, benzol and carbonic disulphide.

The *chloride* fell as a white precipitate on adding hydrochloric acid to an alcoholic solution of the base; microscopic rhombic and prismatic plates apparently monoclinic, slightly soluble in water, alcohol and glacial acetic acid, insoluble in ether and carbonic disulphide; melting-point 288°.

Diparachlorbenzylamine Chlorplatinate, $[(C_6H_4ClCH_2)_2NH_2]_2PtCl_6$, made by adding aqueous chlorplatinic acid to the alcoholic solution of the base, and purified by washing with water, was dried at 100°, and analyzed.

0.2389 gram substance gave 0.0496 gram platinum.

	Calculated for $[(C_7H_6Cl)_2NH_2]_2PtCl_6$.	Found.
Platinum,	20.90	20.76

Properties. Pale yellow scales (deeper in color than the corresponding salt of the tertiary amine), slightly soluble in boiling water, almost insoluble in cold water and alcohol.

The *bromide* of the base was obtained during the preparation of the amines in white scales very slightly soluble in water or alcohol, insoluble in ether, easily decomposed by aqueous sodic hydrate, and melting with decomposition between 280° and 290°.

The salts just described are identical with those of the α modification of Berlin's secondary chlorbenzylamine; and, as we could find no trace of any other modifications, there can be but little doubt that the β, γ and δ forms of Berlin consisted of mixtures of para- and ortho-compounds, in varying proportions, and this view is still further supported by the fact that the melting-points of these so-called isomeres are very near together, those of the chlorides in fact all lying within ten degrees.

Monoparachlorbenzylamine, $C_6H_4ClCH_2NH_2$, precipitated from the aqueous solution of its bromide with sodic hydrate and distilled with steam forms a colorless oil nearly, if not completely, insoluble in water, but soluble in ether; on exposure to the air it is converted, almost at once, into a white soluble crystalline carbonate; if therefore care is not taken to exclude carbonic anhydride, small quantities of the amine seem to dissolve easily in water.

The *carbonate* was made by exposing the free base to carbonic anhydride or even to the air, and was always left when an ether extract containing the base was allowed to evaporate spontaneously. Crystallized from water, it forms white plates often of considerable size, from alcohol needles; melting-point, 114°–115°; it dissolves slowly in cold, quickly and freely in hot water and alcohol; sodic hydrate sets free the oily amine.

The *chloride* made by dissolving the carbonate in hydrochloric acid crystallizes in long, narrow white plates, soluble in water and alcohol, sparingly soluble in glacial acetic acid, and essentially insoluble in ether, benzol and carbonic disulphide; melting-point, 239°–241°.

Monoparachlorbenzylamine Chlorplatinate, $(C_6H_4ClCH_2NH_3)_2PtCl_6$, made by mixing a solution of the chloride of the base with platinic chloride, purified by washing with a mixture of alcohol and ether, and dried at 100°, gave the following result:

0.3067 gram substance gave 0.0866 gram platinum.

	Calculated for $(C_7H_6ClNH_3)_2PtCl_6$.	Found.
Platinum	28.39	28.23

Properties. Bright yellow branching plates or needles, arranged in round woolly groups when crystallized from water, in which and alcohol it is decidedly soluble.

The *bromide* of the base formed in the preparation of the amines resembles the chloride in appearance and solubility, but is somewhat less soluble in cold water, and melts with decomposition between 225° and 230°.

The foregoing results differ from those obtained by Berlin only in the melting-point of the chloride, which he found 197°; he gives no melting-points for the carbonate and bromide.

To make it easier to compare the new melting-points with those in use heretofore, we have collected them in the following table; the second column of which gives the melting-points of the pure substances made by us, and the third the melting-points determined by the chemists mentioned in the fourth column.

Name of Substance.	True Melting-point.	Old Melting-point.	Authority for Old Melting-point.
Parachlorbenzylchloride	29°	Liquid.	Beilstein and Geitner.
Parachlorbenzylbromide	48½°		
Parachlorbenzylalcohol	70½°	66°	Beilstein and Kuhlberg.
Parachlorbenzylcyanide	29° (?)	Liquid.	Neuhof.
Parachloralphatoluylic Acid	103½°-104°	60°	Neuhof.
		68°	Radziszewski.
Parachlorbenzylsulphocyanate	17°		
Primary Amine	Liquid.	Liquid.	Berlin.
" " Chloride	239°-241°	197°	"
" " Bromide	225°-230°		
" " Carbonate	114°-115°		
Secondary Amine	29°	Liquid.	Berlin.
" " Chloride	288°	288°-289°	"
" " Bromide	280°-290°	283°-299°	"
Tertiary Amine	78½°	88°-89°	"
" " Chloride	196° (?)	170°-175°	"

The revision of the parachlorbenzyl compounds will be continued in this laboratory; in fact, the aldehyde and some of the sulpho-derivatives have been already made and partially studied by Mr. J. Fleming White, whose work will form the subject of a later paper of this series.

ON THE ACTION OF HYDROCHLORIC ACID AND OF CHLORINE ON ACETOBENZOIC ANHYDRIDE.

By Wm. H. Greene.

In a note published in the *Bulletin de la Société Chimique* (32, 164), M. Loir states that acetobenzoic anhydride prepared by the action of benzoyl chloride on sodium acetate is decomposed by hydrochloric acid at 130°, into acetyl chloride and benzoic acid, while at 140° chlorine converts it into acetyl chloride and chlorobenzoic acid; under the same circumstances the anhydride made by the reaction of acetyl chloride with sodium benzoate yields nothing, but at 160° hydrochloric acid converts it into benzoyl chloride and acetic acid—with chlorine at 170° it yields benzoyl chloride and chloracetic acid.

These reactions appeared extremely improbable. Acetobenzoic anhydride begins to decompose at a temperature below 150°, into acetic anhydride and benzoic anhydride; at temperatures near this point it should act with reagents as would a mixture of the two

anhydrides. Besides this, M. Loir determined the nature of his decomposition products by putting them in water, and did not, it appears, attempt to fractionate his distillates in any manner. Acetic anhydride is decomposed by hydrochloric acid at ordinary temperatures, and acetobenzoic anhydride, a less stable compound, would hardly withstand the action of the same reagent at temperatures near 100°.

I have repeated the experiments of M. Loir with the following results:

If dry hydrochloric acid be passed into acetobenzoic anhydride at ordinary temperatures, the reaction is the same, by whichever process the anhydride may have been prepared; benzoic acid is deposited, and the tube conveying the hydrochloric acid becomes obstructed. On raising the temperature, acetyl chloride begins to distill at 55–60°, and the product obtained up to 130° is a mixture of acetyl chloride and acetic acid. If the heat be raised much above 130°, and the current of hydrochloric acid rapid, a small quantity of benzoyl chloride is carried over, and will be found in the distillate. The residue in the apparatus consists of benzoyl chloride and benzoic acid. If the anhydride be heated to 130°, or any other temperature, before passing the hydrochloric acid, the reaction is the same with the anhydride prepared by each process. However, it seems that the lower the temperature the greater the proportions of acetyl chloride and benzoic acid which are formed, while at higher temperatures (130–150°) the reaction yields acetyl chloride, acetic acid, benzoyl chloride and benzoic acid in about equivalent proportions.

Chlorine acts in an analogous manner; the products are the same in whichever manner the anhydride may have been prepared; but, with the exception of the acetyl chloride, these products are more difficult to separate than those formed in the reaction with hydrochloric acid. Indeed, chloracetic acid boils at about 186°, and benzoyl chloride at 198°; yet, in the experiments of M. Loir, the latter compound seems to have distilled over first, leaving the chloracetic acid in the retort. At temperatures near 150° the products of this reaction are acetyl chloride, chloracetic acid, benzoyl chloride and o-chlorobenzoic acid; at lower temperatures the principal products are acetyl chloride and chlorobenzoic acid.

From his experiments M. Loir concludes that the constitution of benzoyl acetate differs from that of acetyl benzoate; but the

results of these experiments being erroneous, such a conclusion is unsustained. The bodies thus named are identical, all of their reactions *under the same conditions* are the same, and they must be represented by the same rational formula.

ON THE RELATIVE DENSITIES OF PERMANENT GASES AT HIGH TEMPERATURES.

By J. M. Crafts.

The ingenious method* of Professor Victor Meyer for the determination of the density of vapors is too well known to need a description, and many chemists have already recognized by personal observation the great value of this addition to our means of investigation. The unlooked-for observation of an abnormal and peculiar density in the case of chlorine and iodine, which appeared in the month of July 1879, added greatly to the interest already excited by a very remarkable and extended series of observations, and the results of V. and C. Meyer have been commented upon from various sides. Sir Benj. Brodie looks upon them as confirming his theoretical views upon the composition of the halogen group; Prof. Lieben† has given them another interpretation, and some doubts‡ as to the accuracy of the conclusions have been expressed, but thus far they have not been justified by experiments having a direct bearing on the subject.

* Ber. deutsch. chem. Gesell. 11, 1867, 2253; 12, 609, 681, 1112, 1195, 1282, 1426, 2204.

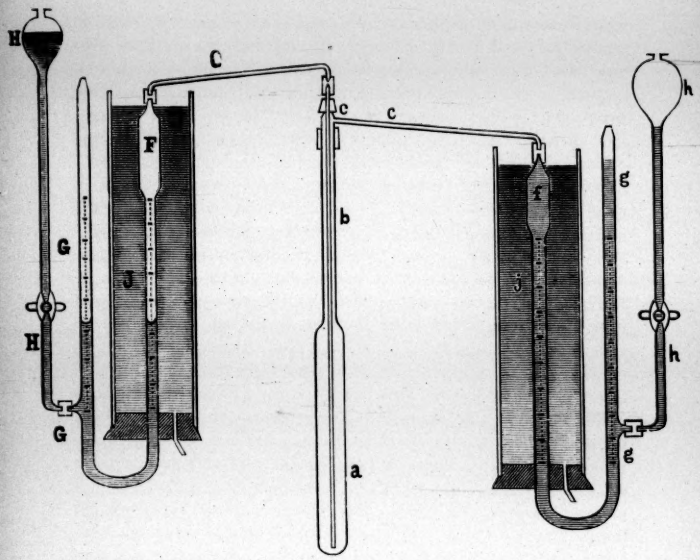
† Comptes rendus 89, 253. Professor Lieben's supposition of an abnormal coefficient of expansion has fewer analogies in its favor than Professor Meyer's idea of a chemical dissociation, when it is borne in mind that the phenomenon to be explained is a ⅔ normal density constant within large limits of temperature.

‡ Ber. deutsch. chem. Gesell. 12, 2066. Professor Seelheim recalls certain experiments upon the volatility of the chloride of platinum in a current of chlorine and proposes the equation $Pt_2Cl_4 = 2Cl_2 + Pt_2 = 6$ vols. as an explanation of the ⅔ density attributed to chlorine. His equation is not in accordance with his own figures, since he says that the volume is increased by ⅓, but the equation would suffice to account for the increase of ½ really observed by Professor Meyer. It would appear, however, desirable to support by some more direct experiment the hypothesis that chlorine (even when mixed with a certain quantity of air as it is in Meyer's apparatus) can maintain in a state of vapor 2.77 times its weight of platinum at a temperature of 1200° and that without the intervention of a permanent chemical combination. Professor Dunnington (Chem. News 40, 141) cites some observations upon the difficulty of obtaining platinous chloride in a state of purity.

In the month of September of last year the author expressed to Professor Meyer his desire to repeat the experiments upon the density of chlorine, and was furnished most readily with information regarding the manufacture of the porcelain cylinders and the precautions to be observed in heating them to avoid fracture. The results of these experiments were communicated to the French Academy of Sciences at the sitting of Jan. 26, 1880, and the subsequent paper of Professor Meyer, which bears the date Feb. 25, 1880,* confirms them in regard to gaseous chlorine. As the methods of operating present some differences, and results have been obtained with a number of other gases, the present memoir describes these experiments in detail. They are confined entirely to gases, and chlorine salts of platinum have not been experimented upon, since the employment of gaseous chlorine simplifies the process and leaves less room for varied interpretations of the results.

The principle of the method is the same as that of Professor Meyer's: namely, the displacement of a known quantity of one gas by another, with the necessary precautions to insure that both gases have been heated to the same temperature. The relative densities are in inverse proportion with the two volumes measured before and after the displacement. The accompanying plate gives the general arrangement of the apparatus; but in order to economize space the furnace is not represented, and the capillary tubes which join the two measuring apparatus with the porcelain cylinder are represented somewhat shorter than the reality; these must be adapted to size of the furnace, and must allow the measuring tubes to be sufficiently distant to be protected by a screen from the radiant heat. In these experiments the porcelain cylinder *ab* was heated in a Perrot's gas furnace in exactly the manner indicated in the design published by Professor Meyer,† except that the bottom of the cylinder *a* was not allowed to touch the clay support, but was held in position by a clamp above the furnace, and this arrangement is a most essential precaution in using enamelled porcelain vessels at a high temperature; the enamel must not be allowed to touch a heated surface to which it may adhere. The stem of the cylinder is much less exposed to this danger, because the current of air through the hole in the furnace cover prevents the enamel from attaining the temperature necessary to its fusion.

* Ber. deutsch. chem. Gesell. 13, 339. † Ibid. 12, 1113.



The ⟦ tube *FGH* serves to measure a fixed quantity of the gas whose density is to be taken. Since the gas is expanded to about six times its original volume at 1350°, and since it should not fill more than two-thirds of the porcelain cylinder, when introduced into it at that temperature, the measuring tube is made to contain from 10 to 14 c. c., when a porcelain cylinder of 100 c. c. capacity is used. For lower temperatures a larger measuring tube may be used. The error in measuring depending upon the variable quantity of liquid adhering to the sides of the vessel *F*, errors of observation and fault of level in the two branches *F* and *G*, does not exceed 0.02 c. c; consequently it amounts to 0.2 per cent. when 10 c. c. are taken. A number of experiments were made to determine this limit of accuracy, and it may be remarked that the use of sulphuric acid instead of water is not unfavorable to constant results. The measuring apparatus was carefully calibrated with water, and a series of experiments which were made by weighing the quantity of liquid,

which the vessel contains under different circumstances (varying the temperature and the time during which the liquid was allowed to flow out) contributed to fix the conditions necessary to obtain constant results. Both branches of the U tube have corresponding divisions to facilitate bringing the liquid to the same level in each. It is only when mercury is used that this operation presents some difficulty. The vessel *H* provided with a cock serves to regulate the pressure, which is kept as nearly as possible equal to the atmospheric during any transfer of gas. *H* communicates with *G* by means of a flexible joint in black caoutchouc, which resists even the action of strong sulphuric acid during several days. The measuring apparatus *fgh* is similar in every respect to the previous one. *F* and *f* are surrounded with water which is changed before each experiment in order to insure that both measuring tubes should be at the same temperature. When the gases are measured over sulphuric acid or mercury it is unnecessary to know the temperature, but sometimes water was used in the tubes *f g*, and then the temperature was measured in order to calculate the tension of aqueous vapor. The tube *FGH* communicates by means of the capillary tube *C* with a platinum tube of about 0.8 mm. interior diameter, which conveys the gas to the bottom of the porcelain cylinder. The piece *cc* allows the displaced gas to flow from the upper part of the cylinder into *f* where it is measured. The joints are made with black caoutchouc of 4 mm. exterior diameter and only 0.7–0.8 mm. interior diameter, and all joints bound with copper wire. The apparatus, when arranged in this manner and attached to a manometer, sustains a vacuum for 24 hours, and frequent trials were made during the experiments to ascertain that all the connections were in good condition.

During all the experiments of the present memoir, as the determination of temperature proved to be little involved in the study of the density of permanent gases, it was thought sufficient to heat the porcelain cylinder directly in the gas flame of the furnace as was done by Professor Meyer, although it is questionable whether an equal distribution of heat is thus obtained. This mode of operating has, however, a serious disadvantage. The enamel of the porcelain is rapidly attacked, particularly on the side where the current of heated gases is most rapid, and the cylinders soon become pervious to hydrogen and to aqueous vapors, but not to other gases. A large number of determinations were made of the quantity of

water which passed through the porcelain during a given time, when it was exposed at a high temperature to the products of combustion, and the quantity was found equal to 0.001–0.002 gram per hour, and accordingly the quantity which penetrates during the five to ten minutes that an experiment lasts is too small to affect the results, but it is essential to fill the porcelain cylinder directly before each experiment with dry gas. There is probably little unburnt hydrogen in contact with the exterior surface of the porcelain, and the diffusion of this gas only becomes noticeable in experiments in which the cylinder is filled with it.

It is only necessary that the temperature should remain constant about five minutes, and that no perceptible loss or gain of gas should occur during that time, to make a determination of density possible under favorable conditions, and usually no experiment was made until the volume of gas in the closed apparatus had remained constant during ten minutes. In order to determine how quickly the interchange of temperature takes place between the cold gas introduced into the apparatus and the heated gas which is displaced, a series of experiments were made with air displacing air, by forcing into the porcelain cylinder 10 c. c. of air, and by detaching the vase *fgh* after a given interval of time to measure the volume of air displaced. It was found that within the limits of error already mentioned the 10 c. c. taken in the apparatus *FGH* were found again in *fgh* after about one minute, and that there was no further change of volume; hence a result obtained after the first minute may be taken as exact, and the very short time required for an experiment enables determinations to be made under unfavorable circumstances, when observations of longer duration would be complicated by phenomena of diffusion and other causes of error. It follows then that the comparison of the density of two gases at any temperature which can be supported by a porcelain apparatus is a very simple and rapidly executed operation.

The details of the process are these: The heated porcelain cylinder is filled with the gas which is to serve as the standard of comparison, by conducting it first in a rapid, and finally in a slow current through the platinum tube until all traces of other gases are expelled. It is usually preferable to choose the lighter of the two gases for this operation, which lasts from five to ten minutes; as soon as it is concluded the rubber connection at the end of the platinum tube is closed, the measuring apparatus *fgh* is attached

to the capillary tube *c*, and observations of the level of the liquid in *f* are made until a constant position, during five minutes at least, indicates a constant temperature.* When the temperature of the furnace is constant that of the porcelain cylinder becomes stationary in two or three minutes, because the slow current of gas which is passed through at the last abstracts very little heat. The level of the liquid in *f* is set at zero, the platinum tube is left open for a few seconds in order that the gas may take the atmospheric pressure, and it is then connected with the capillary tube *C*, and a known volume of gas, measured in *F* also under the atmospheric pressure, is forced into the porcelain cylinder, and the corresponding volume of gas displaced is measured in *f*, taking care to regulate the outflow of the liquid so that the level is the same in the two branches. It is easy to test and correct an error from this source by noticing the change of level, if any, that takes place on allowing *f* to communicate again with the air. The diffusion of the two gases destroys the value of the comparison between their densities after a few minutes, but if their coefficients of expansion are the same, which appears to be nearly the case in all the permanent gases that have been thus far examined, no difference in the results is apparent. In the case of chlorine several analyses were made of the gas which had passed over into the measuring tube *f*, and it was found after about five minutes to contain two or three per cent. of chlorine, so that if the density had proved decidedly abnormal, as seemed at first possible from Professor Meyer's researches, it would have been necessary to have taken this quantity into consideration.

It is scarcely necessary to add that the gases operated upon must be perfectly dry, and consequently water can only be employed in the measuring tube *fgh*, and it is usually more convenient to fill both tubes with sulphuric acid or with mercury.

The following experiments were made with chlorine prepared in the usual way with peroxide of manganese, that had been left several days in contact with hydrochloric acid to decompose carbonates. The flask was not heated higher than 25° during the evolution of the chlorine. It is easy to measure this gas over sulphuric acid, and the

*The changes of temperature of the gases in these operations are extremely rapid and are probably nearly completed in the capillary tubes, so that the gas which reaches the bottom of the porcelain apparatus and that which passes out through the tube *c* have nearly acquired the temperature which they should have at the moment of measuring them. The low specific heat of gases enables them to assume the temperature of the surface layer of the material enclosing them, and this property is very favorable to the performance of these determinations of density. 23 grams of glass in cooling one degree heat 10 c. c. of a gas to 1300°.

only precaution necessary is to expose the acid in the measuring tubes during one or two hours to an atmosphere of chlorine in order that the slight absorption, which takes place, may be complete. As the liquid is not afterwards agitated in presence of the gas, no appreciable absorption or disengagement takes place. Chlorine attacks black rubber very slowly, and diminution of volume is observable from this source after a few minutes; but, rejecting the first experiment in which fresh surfaces are exposed, the subsequent ones gave approximately accurate results. The platinum tube is not readily attacked in the parts which are cold nor in those which are strongly heated; but a zone of one to two centimeters in length, which has a temperature of 400 to 500°, is more rapidly attacked; and although the tube is not actually eaten away, the passage of a current for several hours makes it brittle and crystalline. It lost about 0.01 gram in weight in half an hour in each of two experiments, the total weight of the tube being about 40 grams.

10 c.c. of chlorine displaced	9.41 c.c. air	1st experiment.
10 " " "	10.43 " "	2d "
10 " " "	10.30 " "	3d "

If the apparatus is filled with chlorine and 10 c.c. of air are introduced the results are less satisfactory, on account of the formation and decomposition of chloride of platinum on the outer surface of the tube, when it is not heated red hot and is exposed to a mixture of chlorine and air of variable composition.

The platinum tube was replaced in the following experiments by a clay pipe stem, deprived of the glazing which hardens the exterior surface, and which often appears to contain lead.

10 c.c. of chlorine displaced	10.37 c.c. air	1st experiment.
10 " " "	10.24 " "	2d "

In order to meet the objection that part of the chlorine had been absorbed by the pipe stem, giving an apparent density higher than the real, the experiment was reversed, and air was passed into the porcelain apparatus filled with chlorine.

10 c. c. of air displaced	9.98 c. c. chlorine.
10 " "	10.00 " "

It will be noticed that these results vary two or three per cent., and leave the question unsettled whether the density of chlorine compared with that of air is exactly normal or slightly less than the

normal density, but they were chiefly undertaken to ascertain whether under these circumstances chlorine would be found to expand one and one-half times as much as air at a high temperature, as Professor Meyer had concluded from his experiments with platinum salts, or whether the density is nearly normal, and these observations amply suffice to resolve this problem. In view of the two-third density which had been found for chlorine it was thought necessary to examine the possibility of the absorption of chlorine by the clay pipe stem, and the subsequent abandonment of the chlorine in the presence of air. Had this phenomenon taken place in two series of experiments above, the absorption of exactly 5 c. c. in the first case and the evolution of 3.33 c. c. in the second case would disguise an abnormal density and give the apparent density stated above. This extremely improbable hypothesis was tested by placing beforehand in the cylinder enough fragments of pipe stem to double the volume of this material, and consequently double its effect. An experiment made under these conditions gave the same results as before, 10 c. c. of chlorine displaced 10.20 c. c. of air.

The hypothesis that chlorine may be a compound of oxygen has been revived and associated with the results of Professor Meyer. The following equation for example, which would explain the two-third density, has been proposed as a guide to further investigations,* $2\,(M_3O_2) = 2\,(M_2O) + O_2$. M represents the hypothetical element, murium. It appeared that hydrochloric acid might give an abnormal density of unforeseen value, according as the hydrogen, favoring this dissociation, combined chiefly with the murium or with the oxygen. A series of experiments was made with pure and perfectly dry hydrochloric acid measured over mercury.

10 c. c. of this gas displaced 10.03 c. c.; 9.93 c. c.; 9.97 c. c. of nitrogen; and 10 c. c. of nitrogen displaced 9.73 c. c.; 9.61 c. c.; 9.68 c. c.; 9.63 c. c.; 9.73 c. c. of hydrochloric acid.

The loss, particularly in the second series where the apparatus was filled with hydrochloric acid, may depend upon an absorption

* Mention is made in a lecture given by Professor Meyer, and reported by Mr. Watson Smith in the *Chemical News* 39, 49, of the production of oxygen by passing chlorine through a heated porcelain cylinder and absorbing the undecomposed chlorine by iodide of potassium. The penetration of aqueous vapor into the heated cylinder may perhaps account for the formation of small quantities of oxygen, according to the equation of a partial reaction $H_2O + Cl_2 = 2\,HCl + O$, as it has been shown that the chlorine would be in presence of water under these circumstances.

with the rubber connections or by the heated porcelain. It increases with the duration of the experiment and amounts to 1 or 2 c. c. in an hour; but these experiments suffice to demonstrate that the density of hydrochloric acid is nearly normal. It is essential to use nitrogen and not air in these experiments at a high temperature, since oxygen causes a partial combustion of the hydrochloric acid, and the loss is increased by 0.2 to 0.3 c. c.

Hydrochloric acid does not act upon porcelain at a high temperature with formation of any gaseous product and serves admirably to expel other gases from the cylinder, its ready absorption by water offering a means of separating it from them. Two experiments in which hydrochloric acid was passed for half an hour through a porcelain apparatus at a bright red heat gave only 0.2 to 0.3 c. c. of gas unabsorbed by water. These facts were taken advantage of from the beginning of these investigations to devise a new and convenient process for the estimation of high temperatures, which will be described later. All the experiments in this paper were made at the highest temperature obtainable with a small Perrot's furnace, and various measures fix it between 1300° and 1400°, but the exact measure of the temperature and the mode of heating acquire far greater importance when the density of a gas varies with the temperature as is the case with iodine, and special attention is devoted to this subject under that head.

The determination of the density may serve as a measure of the dissociation of those gases which combine with diminution of volume, and consequently are decomposed with augmentation of volume, like steam, carbonic acid, ammonia, &c., and experiments were made with carbonic acid to ascertain whether dissociation could be detected by this means at 1300°–1400°.

10 c. c. of carbonic acid displaced 10.03 c. c., 10.01 c. c., 10.00 c. c., 10.03 c. c., 9.95 c. c. and 10.09 c. c. of nitrogen.

10 c. c. of nitrogen displaced 9.95 c. c., 9.91 c. c., 9.98 c. c. and 9.93 c. c. of carbonic acid.

In this case in which the gases operated upon do not attack the rubber connections, and are not affected by moisture, the results correspond very closely with each other, and show that if dissociation takes place under these circumstances it is to a very slight extent.

The difference of density noticed may be attributed to a different coefficient of expansion, and the first series of experiments shows

that the 10 c. c. of carbonic acid occupy at 1350° 1.002 times the volume that 10 c. c. fill at the same temperature. The second series of experiments gives the number 1.005 as the value of the same relation. If the coefficient of expansion of nitrogen is 0.00367, that of carbonic acid is 0.003677–0.003688 between 0° and 1350°. The coefficient of expansion of carbonic acid between 0° and 100° at a constant pressure has been determined at 0.00371 by Regnault,* and a diminution of this value as the temperature is farther removed from the boiling point of carbonic acid, until a constant coefficient equal to 0.00367 is reached, would give the mean coefficient observed in the above experiments.

A long interval of temperature diminishes proportionally the importance of numerical errors, and if the means of investigation were equally exact the coefficient established above would have a probable error 13.5 times smaller than that obtained between 0° and 100°; and although it is probable that various causes diminish the value of results obtained at high temperatures, it is to be noticed that the single experiments, and even the two series compared with each other, are as concordant as the experiments of Regnault; but these observations are not regarded as conclusive upon the coefficient of dilatation of carbonic oxide, and experiments will be undertaken by a different process to control this important factor.

A number of experiments were made with hydrogen which have not given precise results because the porcelain cylinder, heated directly in the flame of the furnace, allows hydrogen to penetrate the enamel. They seem to point to a lower coefficient of expansion for hydrogen than for nitrogen; further experiments will be made upon this subject with different modes of heating.

The only other permanent gases with which it is possible to make experiments with this apparatus are the oxides of carbon and compounds of nitrogen. The oxides did not seem likely to offer any new features of interest, but some observations were made upon the decomposition of ammonia which will be described in the next paper.

* Mémoires de l'Académie, 21.

THE VAPOR DENSITY OF IODINE.

By Fr. Meier and J. M. Crafts.

The memoir of V. and C. Meyer,* referred to in the preceding paper, contains the statement that the vapor density of iodine presents the same curious anomaly which they found for chlorine, namely a constant density equal to two-thirds the normal at all temperatures above 1000°–1200°, and consequently they look upon this phenomenon as confirming their original views regarding the constitution of chlorine. At that time no distinction had been made between chlorine employed as a gas or disengaged from a platinum salt; and since one of us had failed to discover a peculiar density for chlorine, it was thought advisable to examine carefully that of iodine, as the case seemed simpler than that of the decomposition of a platinum salt.

This work was ready for publication before the appearance of the last paper of Professor Meyer,† in which he finds two distinct densities for chlorine, and gives a series of determinations of the density of iodine at different temperatures. The work with gaseous chlorine by a modified process is nearly in accordance with the results described by one of us, but our results with iodine differ notably from those of Professor Meyer, and we do not regard them as confirming his theoretical views. We venture therefore, after consulting with him, to place our results beside his with the details necessary to a comparison of our different methods of operating, which may perhaps suffice to explain the differences in our conclusions.

When the investigation was first undertaken it seemed to us especially important to seek for the cause of the different value, which is obtained for the vapor density of iodine by the method employed by MM. Sainte Claire Deville and Troost in their classic research‡ which extended so greatly the range of experiments in this direction. They found the vapor density of iodine normal at 860°–1040°, and used it as a standard of comparison for the determination of other densities. Since the publication of the results of V. and C. Meyer, and also of a brief abstract§ of those

* Ber. d. d. chem. Gesell. 12, 1431.
† Ber. d. d. chem. Gesell. 13, 399.
‡ Annales de Chim. et de Phys. 58, 257.
§ Comptes rendus.

contained in the present paper, which we communicated to the French Academy of Sciences, M. Deville* has modified his apparatus for obtaining a constant temperature, and proposes to repeat the experiments with iodine. It is best therefore to withhold all speculations upon this question until this work is completed.

The manner in which Professor Meyer has grounded upon his experimental data some most ingenious hypotheses appears to us to add greatly to the interest of the question, and believing that we do not misconceive his intentions in regarding these views rather as guides to further research than as definitely established theories, we desire to discuss them with reference to their probable value in supporting and co-ordinating his facts. We have not repeated the experiments with chloride of platinum, which led Professor Meyer to the molecular weight 47.3 for chlorine at high temperatures, but our views regarding the question are influenced by our failure to obtain similar results with iodine, which according to Professor Meyer presents the same phenomenon of a density equal to two-thirds the normal.

The nascent state of chlorine set free from platinous chloride and the hasty ("brusque") volatilization of bodies are offered† as an explanation of the difference of density between chlorine from platinous chloride and chlorine employed in the gaseous state, and the rapid heating of solid iodine is supposed to be a partial explanation of the difference of density obtained by Meyer's or Deville's process. It appears to us doubtful whether the term nascent state can be applied to a condition which subsists during several minutes at 1500°. The conception, which at the best is somewhat vague, of the nascent state has been evoked to explain some chemical phenomena in which it is usually possible to attribute an important part to the influence of the mother substance — influence which extends throughout the duration of the reaction. Here, however, the chlorine must be considered as removed from all influence of the platinum as soon as it acquires the gaseous state. It is possible to conceive a distinction between chlorine born of a union with a noble metal like platinum, and ordinary chlorine; and this point of view has analogies with that of Schönbein for ozone and autozone, but only, as it appears to us, when the phase through which the density of chlorine passes at about 700° is disregarded. Oxygen is disengaged from certain com-

* Comptes rendus, 90, 773.

† Ber. deutsch. chem. Gesell. 13, 401.

pounds as ozone, and retains its peculiar molecular weight so long as it remains ozone; but according to Professor Meyer chlorine from all sources has a normal density at about 700°, and the abnormal density only appears at higher temperatures. Chlorine must pass through the temperature of 700° to arrive at a higher, and it does not appear why the molecules which have reached a normal density (molecular weight) at 700° should be dissociated in one case more than another, supposing that this stage may be taken as a new point of departure. If it is insisted, upon the other hand, that differences in the constitution of chlorine are produced by a more or less rapid decomposition of its platinum salt, it may be objected that by varying the size and the material of the vessel containing it, which is thrown into the porcelain cylinder, the disengagement of the chlorine may probably be rendered as slow at 1200° as at 700°, and a further experimental development of the hypothesis seems desirable from this point of view. It would be interesting, for example, to ascertain if liquid chlorine, very rapidly heated, would have an abnormal density. An affirmative result would give an important confirmation to Professor Meyer's views, but it must be added that a negative one would not suffice to invalidate them.

Some thirty experiments made with iodine have not revealed anything which would induce us to suppose that iodine changes its density according to the rapidity of its volatilization, but the condensation of the substance in the stem of the porcelain cylinder opposes an obstacle to experiments of long duration, and this reason obliged us to abandon the study with this body of the interesting question of the function of time* in a very simple phenomenon of dissociation.

The iodine used in the following experiments was purified by the method described by M. Stas, except that instead of being simply

*The study of such questions is much easier in the case of permanent gases, and although thus far we have not been able to observe with them a phenomenon of dissociation, one of us has made a few experiments upon the rate of decomposition of ammonia by introducing this gas into a porcelain cylinder heated bright red hot. In the first experiment the cylinder was filled with pure nitrogen and 10 c. c. of ammonia were introduced; after one minute the volume of nitrogen displaced was 10.4 c. c.; after three minutes, counted from the commencement, the volume was 10.53 c. c.; after five minutes it was 10.60 c. c. and after seven minutes it was 11 c. c.

In a second series the cylinder was completely filled with ammonia, and the volume read. After one minute an increase of volume equal to 5 per cent. of the whole was observed.

These experiments were not carried further with the apparatus described in this memoir, because it appeared preferable to make them with an air thermometer with capillary stem, so mounted as to enable the pressure or the volume to be measured at will.

digested with iodide of potassium, it was heated several hours at 150° in a sealed tube with a concentrated solution. The addition of water gave several fractional precipitations from the solution in iodide of potassium, which were collected separately; the first four gave identical results, and only the first three were used in the subsequent determinations of density. Each portion was distilled with steam, dried over nitrate of calcium* rectified several times over anhydrous baryta and sublimed. The iodine thus obtained solidifies at 112.7°–113° (with correction) when the thermometer is immersed in the liquid. The correction for the part of the stem of the thermometer which is not heated is easily made by plunging it to the same point in the vapors of boiling water.

Determinations of the density of this iodine made with a glass apparatus in boiling sulphur give results corresponding exactly with the calculated density 8.786 if certain precautions are taken, the necessity of which will be best appreciated on considering the results obtained under different conditions.

The form of apparatus which we consider preferable is one similar to an air thermometer with constant pressure, and the process consists in introducing the weighed substance into the apparatus, which is hermetically closed before the operation begins, and then measuring the increase of volume corresponding with the volatilization of the substance.

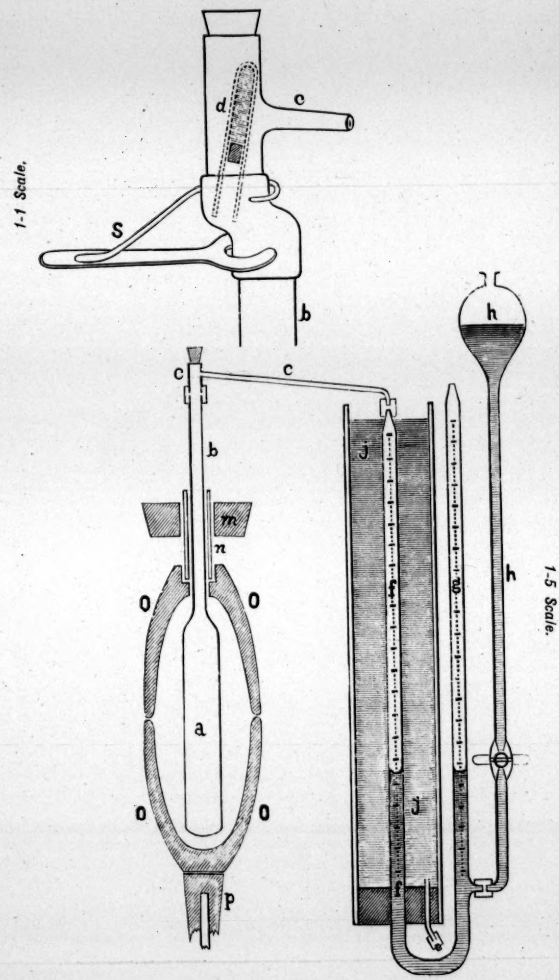
We give only the drawing of the apparatus intended for use at high temperatures, which will suffice to explain the general arrangement adopted in all cases. For experiments in boiling sulphur an iron tube, closed at its lower extremity, is substituted for the parts *m*, *n*, and *o*. This tube is 60 cm. long, 5 cm. wide, and has an iron collar about 35 cm. from its lower end, which supports it in the heating apparatus. This latter consists of two concentric cylinders to prevent loss from radiation, with a chimney on the side, and a Bunsen's lamp is so arranged at the bottom that the flame is not deflected by drafts. A series of holes in the upper part of the inner cylinder allows the equal exit of the air on all sides. It is easy to keep the sulphur boiling, so that the condensation is complete at about 10 cm. below the top of the iron tube, which is closed with a cork through which the stem of the glass cylinder passes. The cylinder *a* is plunged in the liquid sulphur, and when the ap-

*M. Stas says that all other modes of drying introduce impurities. We doubt if they would have affected our results, but the method was adopted to exclude all possible sources of error.

paratus is well arranged it is easy to maintain a temperature so constant that the change of volume in the measuring tube *f* does not exceed 0.01 c. c. during ten minutes. The form of the cylinder *ab* has considerable influence upon the results, and we have made a series of experiments to determine what are the most favorable dimensions. It appears from these experiments that the shape of the lower part *a* is of little consequence, provided it can be heated equally in all parts, since the vapors even in a cylinder of large diameter act during the first few moments like a piston and drive the air out before them, then the diffusion becomes more noticeable, and must be retarded as much as possible by a long narrow stem. The cylinders which we eventually found the most convenient had a capacity of about 150 c. c. The part *a* was about 4 cm. wide and 13 cm. long, and the part *b* was 40 cm. long and 3 to 4 mm. wide (interior diameter).

The following experiment demonstrates to what point the observations can be prolonged before they are vitiated by the diffusion and subsequent condensation of iodine. 0.1266 gram of iodine was volatilised in such an apparatus, and the volume of air displaced measured in the tube *f* was equal to 12.48 c. c. after two minutes; after three minutes (counting from the beginning) 12.52 c. c.; after four minutes 12.51 c. c.; after five minutes 12.49 c. c.; after eight minutes 12.47 c. c.; after 25 minutes 11.59 c. c. The beginning of the diminution of volume usually coincides with the appearance of a slight cloud of iodine vapor in the stem above the mouth of the iron tube.

It is evident that the apparatus *fgh* can be closed at any moment and removed to read the volume at leisure, but it is unnecessary to allow a considerable time to elapse before making the reading, as it was determined by direct experiments that the gas in *f* did not require more than a minute to take the temperature and the tension of aqueous vapor from the surrounding water. The use of a long narrow tube, whose sides are constantly moist, favors the rapidity and accuracy of these observations. It may be here noticed that the formula employed by Professor Meyer to calculate his results presupposes the air in the cylinder *ab* to be perfectly dry, and it is necessary to provide that it is actually so by the careful introduction of dry air before each experiment, otherwise a considerable error may ensue according as the atmosphere is more or less moist. It is important to melt the substance in the


1-1 Scale.
d
c
S
b
c
c
b
m
n
O
O
a
O
O
P
J
J
h
h
1-5 Scale.

little cylinder *d* before weighing it, and to direct the opening downwards in order that the jet of vapor which issues from it may not be turned toward the stem *b*. The accompanying sketch represents the apparatus as arranged for an experiment at the highest temperature in a Perrot's furnace, and in the description we will give in detail the reasons which induced us to modify the original form proposed by Professor Meyer.

The capillary tube *c* communicates freely with the measuring tube *f*, while in the original apparatus the gas was obliged to pass through a layer of water to enter the measuring tube, and the friction and capillary resistance of the water in the tube *c* occasioned loss. In order to estimate the importance of this source of error we arranged an apparatus precisely as described in the *Berichte*, 11, 2254, and forced into the cylinder *ab* 10 c. c. of air without heating. Only 9.5 to 9.65 c. c. of air were forced out of the cylinder into the measuring tube, and it was found that it required an excess of pressure of 6 to 10 cm. of water to make the gas flow out through the capillary tube *c*, although this was only plunged 1 cm. below the surface of the water. This loss of gas does not necessarily occasion an error in the ultimate result, when operating in the manner described by Professor Meyer, as we shall explain later; but his apparatus does not indicate readily a change of tension of the heated gas, and consequently is not very sensitive to changes of temperature.

It is easy to find the correction for the quantity of air displaced by the cork *e*, particularly when it is so small that the volume in question does not exceed 0.2 c. c.; but we have observed an error, which arises when the apparatus is closed at the moment that the vase *d* with the substance is allowed to fall into it, and which appears not to have been noticed by those who have thus far used the process, and a long series of observations which we had made at high temperatures are rendered of little value by this error. We were led to its discovery by certain indications which made us suspect the accuracy of our results, and its nature is sufficiently evident from the following experiment. If the little cylinder *d* without any volatile substance is allowed to fall into the heated cylinder *ab*, and the stopper put in its place as quickly as possible, an increase of volume of 0.4 to 1.0 c. c. is obtained, according to the temperature and the size and material of the vase. If the stopper is put in its place before the vessel *d* is allowed to fall into *ab*, a sudden eleva-

tion of the liquid in *f* may be observed while *d* is falling, consequently there is an inward current of air at that instant, which is quickly succeeded by the inverse movement, which proceeds more slowly until the liquid has fallen to its original level after a minute or a minute and a half. Thus in the ordinary manner of making a density determination air enters while the substance is falling and before the cork is put in. The air is probably in part forced in by the passage of the falling body through the tube *b*, but the sudden cooling of the air in *a* seems to contribute still more decidedly to this effect, at least the quantity of air that enters seems to depend more upon the temperature and the weight of the cylinder *d* than upon its size. The error from this source is so nearly a constant quantity that it is possible to determine its value for fixed temperatures and constant conditions by making experiments with a vessel containing no substance, and the results can be applied as a correction to series of determinations of density made under the same conditions, and we give further on a number of results corrected in this way.

The two errors mentioned are in inverse direction and tend to compensate each other in Professor Meyer's experiments at a high temperature, while at lower temperatures they have little influence on the results, whenever it is possible to discriminate between the two phases of the process and reject the first few bubbles which are disengaged immediately after closing the apparatus, but in the present case it has been thought preferable to remove all causes of uncertainty by modifying the apparatus. We suppose that these differences in the mode of operating, and probably others that we have not recognized, may explain the differences in our results. We believe that Professor Meyer has made some experiments with a closed apparatus, and he communicated to us several methods of allowing the cylinder *d* to fall after the cork has been put in its place, and according to our views such determinations should give too low results because the gas was still obliged to pass through a layer of water. This communication was made after all our experiments were made, and as our form of apparatus differs from that proposed we will describe it in detail.

The part *cc* which is connected with the stem *b* by means of a caoutchouc tube is pushed aside by a sort of key *s*, so that *d* is supported by *b*; the apparatus is thus closed, the position of the water in *f* is read, and the substance tube *d* is allowed to fall into

the heated cylinder by a movement of the key *s*, which is immediately returned to its first position, and the second reading taken which corresponds to the air displaced by the vapors. This arrangement appears to us the one which best accomplishes its object without change of volume or leakage. For high temperatures the iodine was weighed in a little closed cylinder of platinum, and a loosely fitting stopper of platinum prevented the substance from falling out when the cylinder was inverted. It is well to make the cylinder *d* rather heavy (2.5 to 3 grams) in order that it may not become sufficiently heated to volatilize the iodine before reaching the bottom.

The measuring apparatus *fgh* is precisely similar to the one described in the last paper, except that the graduated tube is not enlarged at the top.

The other changes which we have made in the process of Prof. Meyer concern the method of heating, and are destined to insure an equal distribution of heat. If a platinum wire be introduced through the whole length of a Perrot's furnace, the light emitted in different parts shows by its intensity that the wire is not equally heated throughout its length, and it appears to us doubtful if a porcelain cylinder can be equally heated from top to bottom in the naked flame whose temperature varies like a Bunsen's flame in different horizontal zones; we therefore chose a furnace nearly twice as large as that employed by Professor Meyer,* and the porcelain cylinder was surrounded by a muffle. That employed at the highest temperatures is represented by the parts *oo* in the drawing. It can be easily made from two French crucibles, the upper one of which is pierced with a hole through which the stem of the cylinder *b* passes. The tube *n* which passes through the cover *m* and fits into the upper crucible protects the stem *b* from the direct action of the flame. The furnace is not represented in the drawing, because, except the difference of size, it is precisely similar to that shown in the plate *Berichte* 12, 1113, and the capillary tube *c* is represented much shorter than the reality, and as with the previously described apparatus the measuring tube must be sufficiently distant from the furnace to be protected by a screen from the radiated heat.

For temperatures ranging from 500 to 900° we employ a lead bath weighing about 11 kilograms, which is heated in a Perrot's

* The inner dimensions of the fire space are in ours, height 275 mm. and width 145 mm.

furnace. The porcelain cylinder is placed inside one of thin iron to protect it from immediate contact with the lead. So large a mass of metal was taken in order to insure an equal distribution of heat. In the course of time the iron tube is oxydized and eaten through at a line sharply marked by the upper surface of the molten lead.

We have made a number of experiments to attempt to establish the degree of temperature which corresponds with a certain quantity of gas burned in a Perrot's furnace, but without being able to do so in a satisfactory manner. Professor Meyer adopted this expedient, using a graduated gas-cock to regulate the supply of gas and taking care to heat always under similar conditions. We measured the gas with a meter which gave the numbers of litres per minute, but the temperatures do not correspond with the quantity of gas alone, but also with that of the air which is passed through the furnace at the same time; thus the temperature frequently falls as the heating is continued because an increased draft from a hotter chimney draws too much air through the furnace, and on the other hand on pushing the furnace to its maximum temperature it is easy to increase the flow of gas beyond the point of perfect combustion and thus obtain a lower temperature, the gas being burnt in part in the lower part of the chimney. We have not been able to devise any means to measure even approximately the quantity of air which is used in a given time, or even to regulate it so as to obtain at will in different experiments identical temperatures. The variations may amount to 100° between 1000° and 1200°. The highest heat obtainable under definite conditions can be fixed more closely. On the other hand we are in perfect agreement with Professor Meyer in saying that the temperature can be maintained sufficiently constant during an experiment, or even during several.

In choosing a method for measuring the temperature we have thought it best not to employ the one founded on the heat imparted to a platinum cylinder, because the differences of form and material in the case of platinum and the additional difference introduced by heating it in an iron cylinder appears to us to leave room for uncertainty whether the temperature measured is really the same as that attained by a porcelain cylinder heated in the naked flame. We have already said that the flame of a Perrot's furnace is not at the same temperature throughout its whole length, and we have

endeavored to remedy as far as possible this defect by using a very large furnace and surrounding the porcelain cylinder with a muffle, and this mode of heating appears to us to give better guaranty for the correct determination of the temperature than one in which a porcelain cylinder 20 cm. long and of about 100 c. c. capacity is allowed to pass from top to bottom of a furnace, and consequently through several zones, while the combustion is very different, and then instead of measuring the temperature by heating on another occasion a platinum cylinder of only 4.5 c. c. capacity in an iron tube* in the same furnace, the operation is performed in the porcelain cylinder.

Our attention was attracted to the details of Professor Meyer's calorimetric experiments by the very high temperatures which he obtained,† and we would remark in this connection that the co-

*The only experiment which we have made to ascertain whether two cylinders, one of iron, the other of porcelain, acquired equal temperatures in the same furnace, gave no indication of a difference. Palladium does not melt in one or the other, although it melts readily in the flame; consequently, this experiment, so far as it goes, offers no positive evidence against the use of an iron cylinder. M. Violle, however, in recent calorimetric experiments, has thought it advisable to heat a block of platinum in a porcelain cylinder placed beside a porcelain air thermometer in a muffle.

†We give some of the latest determinations of high temperatures to serve as points of comparison:

1877	Violle, Comptes rendus	85, 543.	Platinum melts at		1779°.
1878	" " "	87, 981.	Palladium	"	1500°.
1879	" " "	89, 702.	Iridium	"	1950°.
			Copper	"	1054°.
			Gold	"	1035°.
			Silver	"	954°.

These results agree well with those of M. Ed. Bequerel, Annales de Chim. et de Phys. 68, 73, who gives the melting point of silver at 960°, and that of gold at 1092°. He supposes platinum to melt at about 1580°.

Bequerel, Annales 68, 114, found the following temperatures to correspond with the color of the light emitted:

500° – 550°	= very dark red.
550°–960°	= orange red.
960°	= yellowish.
1100°	= yellowish white.

M. Deville, Comptes rendus, 56, 195, gives the melting point of platinum at 1900°, and considers white heat obtained by burning gas retort carbon with an artificial draught to be 1100°–1300°.

Deville, Annales, 58, 301, says that 1162° is almost white heat, at which the most infusible cast iron becomes liquid.

Valerias, Acad. Belge. Bull. 2, 38, 1874, gives the following as the theoretical limits of the heat of combustion:

Hydrogen	burnt in air	= 1254°.
Oxide of carbon	" "	= 1430°.
Ethylene	" "	= 1612°.

It is evident that the theoretical temperature cannot be nearly attained in a process of combustion, but on the other hand it is to be remarked that these temperatures are estimated from zero as the initial temperature, and that the heat obtained with previously heated gases is

efficient of specific heat of platinum which he employs is lower than that which was obtained by M. Violle in the latest work on this subject. For example, it appears from the data in the *Berichte*, 12, 1428, experiments F 1 and 2, that the coefficient used in calculating the highest temperatures was 0.03938, but if the formula ($C_{t}' = 0.0317 + 0.000006t$), which was established by M. Violle to represent the mean specific heat of platinum between 0 and 1100°, is extended to 1500°, the value 0.0403 is obtained, and if it is used in the calculations of Professor Meyer a lower temperature by about 50° is obtained. This result is probably still too high, as the specific heat of platinum probably increases still more rapidly as its point of fusion is neared; and the same may be said of the number given by M. Violle for the melting point of palladium (1500°), which is to be regarded as too high for a similar reason. We used this point as a test of temperature and convinced ourselves by a number of experiments that palladium* could not be melted in a porcelain cylinder heated in the manner described by Professor Meyer in a Perrot's furnace, although this metal melts readily in the flame; we conclude that the temperature does not reach 1500°, and in our first series of experiments with the smaller furnace we have not reached 1400° in our measurements with an air thermometer.

We will describe in detail the process which has been employed by us during the last three months for measuring temperatures, and of which a brief notice has been published;† it is identical in principle with that which Professor Meyer has used in his latest investigation to compare the density of two gases, and indeed if the capacity of the apparatus employed by him were determined,

greater, but it can not be calculated with our present knowledge of the laws of dissociation and of the specific heat of gases combining with condensation.

Rosetti, Deut. chem. Ges. 10, 2054, gives determinations of temperature in different parts of a Bunsen's flame 17 cm. long which agree tolerably well with the calculated numbers.

Colorless flame mantel	1350°
Violet zone	1250°
Inner blue flame	1200°

These measurements were made with an electric pyrometer graduated by comparison with specific heat determinations, but it is obvious that the high temperature obtained by burning heated air and gas in the outer flame mantel depends upon the form of the flame, and a temperature high enough to melt platinum may be obtained with a good blow-pipe flame. The lower part of the flame corresponds to the heated iron tube in a hot air blast furnace. M. Debray says that platinum can even be melted in the flame of a candle.

* We are indebted to the kindness of M. Debray for a piece of perfectly pure palladium.

† Comptes rendus, March 15, 1880. In this communication we omitted to state that nitrogen and not air was used at high temperatures.

the temperature could be calculated from his published results. The method consists in filling the porcelain cylinder *ab* with dry nitrogen, and as soon as the gas has taken the temperature of the apparatus, it is expelled by another gas and collected in a measuring tube. It is essential to choose for this purpose a gas which can be easily separated from nitrogen, and we have used successfully carbonic acid and hydrochloric acid, and give the preference to the latter, because its instantaneous absorption by water marks well the moment when the operation is finished. It required about two minutes to expel the nitrogen, and the current of hydrochloric acid is continued two minutes more by way of precaution, after which the porcelain cylinder is filled again with nitrogen or air, and is ready for a determination of density. The platinum tube shown in the plate of the preceding paper is used to introduce the gases, and the capillary tube *c* is exchanged for one with the end bent upwards to disengage the gas under a graduated tube standing in water. The platinum tube must be introduced and withdrawn very slowly to avoid presenting a cold surface to the heated porcelain or the reverse, and at the highest temperatures a vibratory movement must be imparted to it to prevent it from sticking to the porcelain. Although the inside of the cylinder is not enamelled, at temperatures above 1250° the surface appears to be enough softened to attach itself to any object presented, and often pieces of half melted porcelain are found hanging to the tube. A fine platinum wire cannot be withdrawn from the cylinder at this temperature, as it breaks with the force required to overcome its adhesion to the porcelain; it is easily detached when cold however, and at the highest temperatures it is often best to introduce the platinum tube after a series of density determinations have been made and not to withdraw it while the apparatus is hot.

In order to calculate the temperature it is necessary to know the volume V which is heated to the temperature T, and also that of the portion of the stem *b* and the capillary tube *c* which are imperfectly heated. This volume v is heated to a series of unknown temperatures, but their total effect upon the volume of air contained in v may be measured by determining separately the nitrogen which is expelled from a precisely similar apparatus under the same conditions. To effect this we use a compensating tube similar to that described by M. Deville for his air thermometer. In the first experiments at high temperatures we had not been able to procure

porcelain tubes closed at one end of precisely the same dimensions as the stems of the cylinders, so that we were obliged to content ourselves with somewhat shorter tubes of Bohemian glass, which penetrated only to the lower surface of the cover of the furnace, so as not to be exposed to a heat that would melt them. We made a series of experiments to assure ourselves that the inner surface of the cover of the furnace marks the boundary between the two volumes V and v, by introducing bits of gold and silver hung from a platinum wire into the stem b and observing the point at which they melted, and we found that the errors in estimating the proportions of V and v in this way were very slight, and subsequent determinations with tubes of porcelain confirmed the results thus obtained. The effect then of the heat upon the volume v which is imperfectly heated is to be ascertained by placing a closed tube of porcelain as nearly as possible beside the stem b of the cylinder, and expelling the air or nitrogen from it with hydrochloric acid as nearly as possible at the same time that the determination of temperature is made with the whole cylinder ab. The capillary tube c and the platinum tube serve for both operations, and it is only necessary to ascertain by a calibration that the capacities of the stem b and the compensating tube are nearly identical and to take into account the variable quantity of air contained in the platinum tube in each operation. The calibration of the total value of air in the whole apparatus abc was usually made by expelling the air at a known temperature (that of the laboratory) with hydrochloric acid, and measuring it in the same graduated tubes used for the other operations; this method is much less troublesome than any other, and has the advantage of rendering the results more easily comparable.

The furnace cover is pierced with two holes for the compensating tube and the stem b, and usually the stream of air which enters the furnace through the ring shaped orifices beside the tubes keeps them from being heated sufficiently to adhere to the furnace cover, but at the very highest temperatures they must be protected with platinum foil.

The following formula is used to calculate the temperature T:

$$T = \frac{V(1 + \beta T) - (A - a)}{(A - a)\,\alpha}$$

V = the capacity in cubic centimetres of the portion of the thermometer which is heated to T degrees.

A = the volume of nitrogen measured at zero which is displaced by hydrochloric acid; consequently A corresponds to the volume of nitrogen heated in $V + v$.

a = the volume of nitrogen measured at zero which is displaced by hydrochloric acid from the compensating tube; consequently a corresponds to the volume of nitrogen heated in v.

$\alpha = 0.00367$ = the coefficient of expansion of nitrogen under constant pressure.

$\beta = 0.000016$ = the coefficient of expansion of Bayeux porcelain.

An actual experiment may serve as an example.

The porcelain cylinder with the platinum tube and the capillary tube c was found by calibration to contain 98.40 c. c. $= V + v$, and a similar calibration of the compensating tube with shorter platinum tube and the same capillary tube c gave the volume $v = 6.00$ $\therefore$ $V = 92.40$. The volume of nitrogen expelled at the temperature T measured over water at 20.5° (bar. 727.9) was

$$21.45 \therefore A = \frac{21.45}{1 + 20.5\alpha} \times \frac{709.9}{727.9} = 19.46 \text{ c. c.}$$

The volume of nitrogen expelled from the compensating tube and reduced in the same way was 4.00 c. c.

With these numbers the approximate value of T was calculated, and 1400 substituted for T in the factor $(1 + \beta T) = 1.0225$ $\therefore V (1 + \beta T) = 94.47$.

$$T = \frac{94.47 - (19.46 - 4.0)}{(19.46 - 4.0)0.00367} = 1392°.$$

The following experiments were made to control the accuracy of the method. A glass apparatus, of which the portion V had a capacity of 120.63 c. c., was heated in an iron tube in boiling sulphur, and the air expelled in the manner described. The value of $(1 + \beta T)$ was taken, equal to 1.0149.

I.	$A_1 = 54.00$ c. c.	$t = 18.0$.	bar $= 725.45$	$\therefore A = 49.58$ c. c.	
	$a_1 = 3.6$	$t = 18.0$.	bar $= 725.45$	$\therefore a = 3.31$ c. c.	$T = 448°$.
II.	$A_1 = 53.95$	$t = 16.6$.	bar $= 725.45$	$\therefore A = 49.81$	
	$a_1 = 3.63$	$t = 21.0$.	bar $= 725.40$	$\therefore a = 3.29$	$T = 445°$.

The true boiling point of sulphur under a barometric pressure of 725 mm. is 445 degrees, so that the second experiment gave an exact result and the first an error of only 3 degrees.

Some determinations were also made of the temperature of a

large lead bath using the above apparatus, and immediately afterwards the form of air thermometer with capillary stem proposed by Regnault, in which the thermometer is closed at the temperature T, and the diminution of pressure is measured when it is surrounded with ice. These results seemed to be satisfactory, but we do not give them in detail because no means exist of proving that the temperatures compared were absolutely identical as in the preceding experiments.

A series of determinations of temperature made with a porcelain cylinder and compensating tube, heated in the manner indicated in the plate, serves to show approximately the relation between the temperature and the number of litres of gas burned per minute in the large Perrot's furnace. The experiments were only made after several hours' heating had established a constant temperature. It will be seen that the highest limit under these circumstances is about 1370°, and the temperature falls when too much gas is burnt. This phenomenon is still more marked with the smaller furnace.

Litres of gas per minute.	Temperature.	*V.*	*A.*	*a.*
29	1190°	87.31	22.63	6.06
37	1371°	87.31	20.71	5.89
60	1331°	87.21	20.63	5.50
80	1318°	87.21	20.72	5.47
80	1352°	87.21	20.40	5.47

We give here the results of the first determinations of density made before we had recognized the necessity of some of the modifications in the apparatus which were made later, in order that the effect of these changes may be noticed in the subsequent experiments.

The column D gives the densities observed; S = the weight of iodine; V = the volume of air displaced; t the temperature of the water in the measuring tube at the moment of reading the volume; bar = barometric pressure corrected to zero. The additional columns $D\ corr.$ and $V\ corr.$ give the densities and volumes corrected approximately for the volume of air which enters at the moment that the substance falls to the bottom of the apparatus and before the stopper can be put in its place. This correction varies according to the temperature and the material of the cylinder d containing the substance. The first series of density determinations

of the vapor of iodine was made by a process as nearly as possible similar to Professor Meyer's, except that the U shaped measuring tube represented in the drawing was employed instead of a measuring cylinder standing over water into which the gas passes through the water.

D	*D* corr.	*S*	*V*	*V* corr.	*t*	*bar.*	*T*	Remarks.
8.55	9.20	0.0619	6.10	5.8	17.0	738.8	446.0°	
8.94	9.26	0.1165	11.68	11.28	24.0	735.9	446.0°	Temperature of boiling sul-
8.48	8.84	0.0832	8.58	8.23	15.5	723 3	445.0°	phur.
8.62	8.92	0.1195	11.95	11.55	14.2	729.2	445.5°	The true density of vapor
8.68	8.98	0.1268	12.58	12.18	14.2	729.2	445.5°	of iodine at this temperature is
8.47	8.81	0.0876	8.93	8.58	14.2	729.0	445.5°	8.786.

The preceding experiments were made with a cylinder of which the body *a* was a little more than 20 cm. long and the stem *b* was 7 mm. wide. The variations result chiefly from the difficulty of heating a vessel of this form in boiling sulphur to a perfectly constant temperature.

D	*D* corr.	*S*	*V*	*V* corr.	*t*	*bar.*	*T*	Remarks.
8.50	8.80	0.0856	8.86	8.46	17.3	733.4	446.0°	Temperature of boiling sul-
8.47	8.75	0.1210	12.41	12.00	17.0	733.0	446.0°	phur.

The cylinder in these last experiments had a wider and shorter body and a narrower stem, and the cylinder *d* containing the iodine was inverted when introduced into the apparatus.

D	*D* corr.	*S*	*V*	*V* corr.	*t*	*bar.*	*T*	Remarks.
8.43	8.74	0.1078	10.84	10.46	12 0°	734.1	335.0°	Temperature of boiling mercury.
8.31	8.72	0.0833	8.50	8.10	12.0°	734.1	335.0°	
8.17	8.73	0.0576	6.24	5.84	19.1°	726.8	394.5°	Temperature of lead bath measured with air thermometer.
8.06	8.69	0.0627	6.79	6.39	19.1°	726.8	394.5°	
8.49	8.81	0.1040	10.65	10.25	13.8°	722.5	445.0°	Temperature of boiling sulphur.
8.49	8.75	0.1293	13.18	12.78	13.0°	723.0	445.0°	
8.46	8.79	0.1043	10.65	10.25	12.7°	723.0	445.0°	
8.44	8.69	0.1340	14.19	13.80	18.0°	716.1	444.5°	
8.29	8.75	0.0631	6.70	6.35	17.1°	724.1	508.0°	Temperature of lead bath measured with air thermometer.
8.34	8.74	0.0722	7.70	7.35	19.3°	723.7	550.0°	
8.11	8.70	0.0604	6.63	6.18	19.3°	723.7	550.0°	

In these last experiments the cylinder *ab* had a capacity of about 130 to 150 c. c., and the interior diameter of the stem *b* was only 3 to 4 mm., and all the precautions which have been recommended

were observed except that of closing the apparatus before allowing the substance to fall into the heated cylinder. It may be noticed that the five experiments in which about 0.1 gram of iodine was taken give very concordant results, and the experiments were frequently repeated, because at that time we were unacquainted with the cause of error arising from not closing the apparatus before beginning the experiment, and we believed that iodine actually had an abnormal density at 445°, and wished to multiply experiments in order to confirm so unexpected a result. The correction for the error in question not only gives a nearly normal density for iodine, but also it tends to give identical results with varying quantities of substance, as it should if its application is justifiable.

D	*D* corr.	*S*	*V*	*V* corr.	*t*	*bar.*	*T*	Remarks.
*6.48	6.84	0.0991	13.10	12.40	11.5	725.8	590°	
*6.45	6.83	0.0997	12.81	12.10	8.8	725.8	610	
7.70	8.33	0.0785	8.98	8.30	18.5	728.5	640	
7.13	7.69	0.0778	9.59	8.90	18.2	728.6	640 / 650	The substance was weighed in a small pipe-clay cylinder.
7.43	8.00	0.0800	9.47	8.80	19.0	731.0	665	
7.55	8.16	0.0781	9.10	8.40	18.5	731.0		
7.94	8.26	0.0928	10.44	10.04	18.0	716.3	670	The substance was weighed in a very thin cylinder of Bohemian glass.
8.02	8.33	0.0948	10.57	10.17	18.0	716.0		
6.49	6.87	0.0931	12.60	11.90	16.5	724.2	850	
6.98	7 32	0.1282	15.51	14.80	11.0	733.7	870	The substance was weighed in a pipe-clay cylinder.
6.67	7.14	0.0839	10.70	10.00	12.0	731.6	890	
6.53	6.87	0.0963	12.40	11.80	10.0	733.4	1040	The substance was weighed in a platinum cylinder.
5.98	6.55	0.0947	13.57	12.90	21.0	728.2	1040	
6.24	6.57	0.0971	13.90	13.20	21.0	727.4	1050	
5.23	5.61	0.0697	11.90	11.10	20.6	725.7	1175	The substance was weighed in a pipe-clay cylinder.
4.92	5.29	0.0628	11.40	10.60	20.5	725.7	1180	
4.72	5.05	0.0664	11.97	11.20	14.5	739.4	1300	The substance was weighed in a platinum cylinder.

All these last experiments were made with a porcelain cylinder having a capacity of about 100 c. c., and the dimensions indicated in the drawing. The interior diameter of the stem *b* was 7 mm. The smaller Perrot's furnace was used, and the cylinder in the last experiment at 1300° was heated directly in the flame, and in all the others it was enclosed in a piece of stout iron tubing closed at one end. The greater number of the corrected densities at the temperatures below 1000° do not differ greatly from those of the series which follows, and which we regard as exact; but we attach little importance to these results, as we have found no means of

* We do not know what error causes these results to deviate from the others.

controlling perfectly the value of the correction applied, and we only publish them in the hope that they may afford a clue to at least a part of the differences which appear between determinations made with the apparatus open or closed at the moment of letting fall the substance. It may also be noticed in this connection that the densities in the last series above 1000° approach more nearly a constant number (equal to about two-thirds the normal density) than in the succeeding series, which, as we have already said, gives the true densities of iodine. One of the causes of this result with the last series is, perhaps, the volatilization of a little iodine at the highest temperatures before the stopper is put in its place, and certain peculiarities in the mode of heating, which require further study, may also have contributed to produce the differences between the two series in question.

The following determinations were made exactly in the way which we have recommended in the earlier part of this paper, and we place the results beside those of Professor Meyer* in order to render a comparison easy. The indications of temperature are not strictly comparable on account of the different methods employed to measure them, but we have placed in the same horizontal line the results, which we suppose to have been obtained at nearly the same temperatures, although the highest, which are probably nearly identical, are estimated by Professor Meyer at 1570°, and by us at 1390°. The substance was weighed in a small cylinder of platinum closed with a platinum stopper, so that it can be inverted on introducing it into the apparatus. The use of platinum, which is not at all attacked by iodine under these circumstances, has the advantage of avoiding all possible error that might occur from the disengagement of gas or moisture condensed upon a porous body when a pipe-clay cylinder is used.

Victor Meyer.				Fr. Meier and J. M. Crafts.			
Temperature.	Density.	$\frac{D'}{D}$					$\frac{D'}{D}$
253°–450°	8.89; 8.83; 8.84; 8.85		1	455°	8.70; 8.78; 8.75		
586°	8.73; 8.71; 8.71						
		0.99	2	677°—682°	8.06; 8.58		0.94
			3	757° 770—765	8.05; 8.28		0.93
840°	6.68; 6.80; 6.80	0.77	4	831°—878°	8.04; 8.11		0.92
1027°	5.75; 5.74		5	1039—1059 1030°	7.18; 7.02; 6.83		0.81
		0.65	6	1270—1280°	6.07; 5.57		0.66
1570°	5.67; 5.60; 5.71; 5.81	0.65	7	1390°	5.23; 5.31		0.60
			8	1468°	5.06; 5.07		0.58

*Ber. d. chem. Gesell. 13, 397.

The details of the above determinations of temperature and density are given below.

	T.				*D.*	*S.*	*V.*	*t.*	*bar.*
1	445	*Temperature of Boiling Sulphur.*			8.70	0.1183	11.70	15.2	735.2
	445				8.78	0.1266	12.49	16.0	731.45
	445				8.75	0.1040	10.20	12.9	728.65
		V.	*A.*	*a.*					
2	677	91.94	31.47	4.8	8.06	0.0873	9.43	15.2	726.0
	682	92.04	31.50	4.8	8.58	0.0983	10.00	15.8	726.0
3	757	92.04	29.47	4.8	8.05	0.1110	12.03	16.0	724.9
	770	91.94	29.11	4.8	8.28	0.1138	12.10	16.7	724.9
	765	91.41	29.11	4.8					
4	831	92.60	27.99	4.8	8.04	0.1164	12.49	12.5	724.2
	878	92.60	27.02	4.8	8.11	0.1068	11.44	14.2	723.6
5	1039	91.70	23.93	4.6	7.18	0.1007	12.18	15.0	728.2
	1059	92.60	23.85	4.6	7.02	0.1008	12.46	15.1	728.2
	1030	90.00	23.74	4.6	6.83	0.1004	12.80	16.0	728.2
6	1270	92.53	20.88	4.2	6.07	0.1135	16.58	20.0	729.1
	1280	92.40	20.76	4.2	5.57	0.0908	14.39	18.8	728.75
7	1390	92.25	19.47	4.0	5.23	0.0729	12.46	21.4	727.7
					5.31	0.0727	12.26	21.6	727.6
8	1468	94.80	20.91	5.73	5.06	0.0521	9.07	18.4	727.65
					5.07	0.0636	11.14	19.9	727.65

The large Perrot's furnace was used, and the cylinder protected by an iron tube, was heated in a lead bath weighing 11 kilograms in the determinations up to 878°; between 1000° and 1390° the arrangement of crucibles represented in the drawing was used, and at 1468° the cylinder was covered with platinum foil and was heated directly in the flame. It will be observed that this temperature is higher than could be obtained by heating directly in the flame of the small Perrot's furnace, and it is possible that not only the larger size of the furnace but also the covering of platinum may have contributed to this result. The familiar experiment of placing a porcelain crucible within one of platinum to increase the temperature, suggests that also under the circumstances mentioned the slighter loss of heat by radiation for the metallic surface may enable higher temperatures to be so obtained. It is proposed to make some direct experiments to ascertain this point.

The only source of error that we have been able to discern in this last series of determinations is the too rapid diffusion of iodine or its projection into the stem *b*, from which results a condensation

and consequent diminution of the volume of air displaced. This error increases the number representing the density, and we suppose therefore that the lowest densities found are the most exact. We conclude from these experiments that the vapor density of iodine compared with air diminishes *progressively* with the increase of temperature between about 600°, when it is still normal, to about 1470°, where it is only 0.58 of the normal density, and we suppose that a still higher temperature than that which we have thus far been able to obtain would give a half normal density. If this phenomenon is attributed to a dissociation, it must be interpreted to mean that the molecule I_2 is separated into two atoms I + I, or else that a group which represents a physical unity is separated into two parts, and we are not disposed to found upon these experiments any new hypotheses regarding the constitution of iodine.

The following table gives the vapor densities of iodine obtained by the essentially different methods employed by MM. Deville and Troost* and by Professor Meyer and ourselves.

Temperature.	Deville and Troost.	Victor Meyer.	Meier and Crafts.
860	8.70	6.75	8.07
1040	8.72	5.75	7.01

The method first proposed by M. Dumas, which was further developed and employed at high temperatures by MM. Deville and Troost, consists in expelling the air from a porcelain bulb by the vapors of a substance heated to a fixed temperature by boiling mercury, sulphur, cadmium or zinc, closing the bulb and comparing the weight of the vapors with that of the air previously contained in it. In the process employed by us the vapors remain mixed with a considerable quantity of air, and it appears probable to Professor Meyer as well as to ourselves that this circumstance may account for a different density in the two cases, supposing that the extent of the dissociation may vary with the tension of vapor, which in our experiments on account of the admixture of air may be one-half, or even less than one-half, that which is attained in the method of MM. Deville and Troost. These authors, however, have published within the last few days a new series† of determinations of the temperatures obtained in the vapors of zinc, which they find to vary according to the mode of heating, and if the new numbers were introduced in the calculation of the density of iodine

* Annales de Chimie et de Physique, 58, 257. † Comptes rendus, 90, 773.

together with those obtained in a subsequent determination* of the coefficient of expansion of porcelain, 7.92 would be the density of vapor of iodine at 940°, which is the corrected boiling point of zinc. Our determinations would indicate 7.6–7.7 as the density at that temperature. The new determination of the boiling point of zinc is much nearer that of M. Ed. Bequerel,† who found it to be 930°; he also fixes the boiling point of cadmium at 746.3°, and if this number instead of 860 were employed in calculating the results of MM. Deville and Troost, the vapor density for iodine would be found higher for this temperature than the number we have given. It is not probable that this rectification of the calculations in question is justifiable, because the boiling points were determined with special reference to the modes of heating used in the experiments with iodine, but they at least show that some uncertainties may exist, and that the new determinations which are promised by MM. Deville and Troost may perhaps give lower densities, and consequently bring them more nearly in accordance with ours. We esteem it fortunate that the question will once more be discussed by these chemists, whose determinations have the highest value, since it is they who have established the general methods of operating at high temperatures, and we desire to reserve our opinion upon the differences in our results until these new determinations shall have been made.

In this paper we have discussed some details of the process of Professor Meyer, because we suppose that the divergence of our results may be explained by differences in our modes of operating, but we are far from wishing to criticise in general his excellent method. We can state in a few words our opinion of its usefulness founded upon the experiments thus far made. The new process invented by Professor Meyer is incomparably more convenient than any of those previously in use. As to its exactness, a number of observations were made by one of us upon an organic body which resists extremely well the action of heat, pure benzophenone, and a series of experiments, made immediately after the first publication of Professor Meyer's process, in which his mode of operating was followed exactly, gave excellent results at temperatures between 355° and the beginning of red heat (about 520°). These experiments, undertaken in order to gain familiarity with the method, showed that it requires little practice to distinguish the two phases of the

* Comptes rendus, 59, 169. †Annales de Chimie et de Physique, 68, 73.

operation; to reject the first bubbles of air, which are disengaged after putting the stopper in its place, and to collect only those which correspond with the vaporisation of the substance.* It may be added that the rapidity and duration of the disengagement of air afford, after a little experience, valuable evidence regarding the stability of the substance and the sufficiency of the heating above its boiling point. Thus the primitive form of the apparatus, which is simpler than ours, appears to us well adapted to solve nearly all the problems in vapor densities that are presented to a chemist, and we do not consider any modification necessary except in the case when it is required to control other experiments, or where a too rapid volatilization, particularly at high temperatures, renders it impossible to separate the two phases of the operation. On the other hand the resistance of the water which enters the capillary tube in Professor Meyer's apparatus prevents it from indicating small changes of temperature, and this imperfect sensitiveness as a thermometric instrument is sometimes inconvenient.

ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

VI.—EXPERIMENTS WITH MESITYLENE.

By Lyman B. Hall and Ira Remsen.

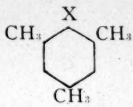
The experiments, an account of which will be given in this paper, were begun more than three years ago, and the principal results were soon reached. Many circumstances have interfered, in the meantime, with the prosecution of the work, and even now it will be seen that perfectly satisfactory conclusions have not been reached. There are some points of fundamental importance which remain to be cleared up, but, as the work involved will necessarily occupy considerable time, and we shall be unable to continue it together, it seems best to give a statement of the results thus far reached and to

*We have already explained that we attribute the good results under these circumstances to the mutual compensation of two errors, that arising on the one hand from the entrance of air during the falling of the vase *d*, and that arising from the incomplete exit of air through the capillary tube.

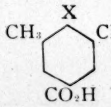
indicate the direction in which the research will be continued. The experiments necessary for a complete and final solution of the problem will, it is hoped, be taken up at the beginning of the next academic year, when, as the road is fairly clear, the desired end will probably be attained in a comparatively short space of time.

In the preceding papers of this series the cases studied have been those in which one substituting group is present in an aromatic hydrocarbon containing two oxidizable groups. It has been shown that when the substituting group is in the ortho position with reference to one of the oxidizable groups, the latter is protected from the influence of chromic acid, whereas the other oxidizable group, whether it be in the meta or para position, is converted into carboxyl.

The question would naturally suggest itself: What will be the effect if the substituting group be in the ortho position with reference to two oxidizable groups, and there be, at the same time, a third in the para position? If we take any mono-substitution product of mesitylene, we have in it the conditions mentioned, and represented in this formula,



in which X may be any negative atom or acid residue. Now, if it is a general law that all oxidizable residues situated in the ortho position with reference to a substituting group are protected from oxidation, when the compound containing them is treated with chromic acid, whereas oxidizable residues situated in other positions are converted into carboxyl, then the result of oxidizing a compound of the formula given above would be an acid of this formula,



which is plainly monobasic.

In order to test the question here involved, the sulphamide of mesitylene was first selected.

Oxidation of Mesitylenesulphamide with Chromic Acid.

The sulphamide of mesitylene was prepared from pure mesitylene by means of the usual reactions and then purified by recrystallization from water. It was treated with the oxidizing agent in the following proportions: 2 grams amide, 14 grams potassium pyrochromate, 20 grams concentrated sulphuric acid diluted with three times its volume of water. The mixture was boiled in a

flask connected with an inverted condenser. The amide gradually passed into solution and the oxidizing mixture changed its color. After boiling for about five hours, a crystallized substance began to separate from the solution while still hot. On cooling, the quantity of this product increased, and corresponded then very closely to the quantity of the amide taken for oxidation. It was filtered off and well washed with cold water, when there remained upon the filter a pure white crystallized substance. The new product was separated from some of the oxidized amide which was still mixed with it by treating it with a cold solution of sodium carbonate. It dissolved very readily, an evolution of carbon dioxide taking place at the same time, while the unoxidized amide remained undissolved. On adding hydrochloric acid to the filtered solution a voluminous crystalline precipitate was formed. This was recrystallized from water two or three times, and then exhibited the properties of a chemically pure substance. The analyses gave the following results:

I. 0.27955 gram gave 0.5306 gram CO_2 and 0.1117 gram H_2O.
II. 0.23275 gram gave 0.4404 gram CO_2 and 0.1066 gram H_2O.
III. 0.26775 gram gave 0.5063 gram CO_2 and 0.117 gram H_2O.
IV. 0.21285 gram gave 0.4024 gram CO_2 and 0.088 gram H_2O.

Analyses 1 and 4 were made with copper oxide; 2 and 3 were made with lead chromate and a mixture of potassium chromate and pyrochromate.

V. 0.3498 gram gave 0.3831 gram $BaSO_4$.
VI. 0.3647 gram gave 0.4006 gram $BaSO_4$.

According to the analyses the mean percentage of carbon is 51.64, that of hydrogen 4.73, and of sulphur 15.05. These results do not correspond to any simple oxidation product of the original sulphamide. The simplest product imaginable, and the one the formation of which was expected, is sulphaminemesitylenic acid, $C_6H_2\begin{cases}CH_3\\SO_2NH_2\\CH_3\\CO_2H\end{cases}$. But a substance of this formula requires 47.16 per cent. carbon, 4.8 per cent. hydrogen, and 13.97 per cent. sulphur, and these figures can certainly not be brought in harmony with those found. On the other hand the results found correspond fairly well with those required by a substance differing from sulphaminemesitylenic acid by containing one molecule of water less, and bearing the same relation to the acid that the sulphinides

described in earlier papers bear to the corresponding acids. The simplest example of this kind of compounds is benzoic sulphinide, $C_6H_4\begin{cases}CO\\SO_2NH.\end{cases}$ The substance under consideration would, according to the principle of nomenclature previously adopted, receive the name *mesitylenic sulphinide*, and its formula is $C_6H_2\begin{cases}(CH_3)_2\\SO_2NH.\\CO\end{cases}$ In the table here given the results of the analyses are placed side by side with those required for mesitylenic sulphinide.

Calculated for $C_6H_2\begin{cases}(CH_3)_2\\SO_2NH.\\CO\end{cases}$			Found.					
			I.	II.	III.	IV.	V.	VI.
C_9	108	51.18	51.76	51.62	51.54	51.53		
H_9	9	4.27	4.43	5.07	4.8	4.6		
S	32	15.16	...	...	...	...	15.02	15.08
N	14	6.64	...	...	...	...	...	...
O_3	48	22.75	...	...	...	...	...	...
	211	100.00						

The results do not agree as closely with those required for the formula as could be desired, but when the difficulty of effecting a satisfactory combustion of a substance containing carbon, hydrogen, oxygen, sulphur and nitrogen is taken into consideration, it will, we believe, be acknowledged that the formula proposed and accepted by us is established by our analyses.

Mesitylenic sulphinide, $C_6H_2\begin{cases}(CH_3)_2\\SO_2NH,\\CO\end{cases}$ is almost insoluble in cold water and with difficulty in boiling water. It is easily soluble in alcohol and ether. From any one of these solvents it may be obtained in crystallized form, though it is best purified by crystallization from water from which it is deposited in the form of short, thick, somewhat irregularly formed, lustrous prisms. It fuses at 255° uncorrected and 262° (corrected).* Like the sulphinides which have already been examined, this one when treated in aqueous solution with carbonates furnishes salts of the corresponding acid.

*Jacobsen (Ber. deutsch. chem. Gesell. 12, 604), who has since prepared this substance, gives the fusing point 259° (corrected 263°).

Calcium sulphaminemesitylenate, $[C_6H_2.(CH_3)_2.SO_2NH_2.COO]_2Ca + 6H_2O$, was prepared by boiling mesitylenic sulphinide and finely powdered Iceland spar together in water. It is easily soluble in water and crystallizes in long, flat, transparent plates. It is also soluble in alcohol.

0.28685 gram lost 0.0523 gram H_2O at 195°, and gave 0.06865 $CaSO_4$.

	Calculated.		Found.
$(C_9H_{10}SNO_4)_2$ ...	456 ...	75.50 ...	...
Ca ...	40 ...	6.62 ...	7.03
$6H_2O$ ...	108 ...	17.88 ...	18.05
	604	100.00	

The *barium salt* is very easily soluble. It crystallizes in groups of very delicate lustrous needles.

Copper sulphaminemesitylenate, $[C_6H_4(CH_3)_2.SO_2NH_2.COO]_2Cu+4H_2O$. This is the most characteristic salt of the acid examined by us. It was prepared by precipitating a solution of the barium salt with copper sulphate. It consists of beautiful, bright blue, small needles which radiate from a centre and thus form groups. These crystals lose water over sulphuric acid after they have been perfectly dried in the air. Placed again in the air, they take up the water rapidly. If, however, all the water of crystallization is driven off by heating to 200° the anhydrous crystals do not take up water by contact with the air. The anhydrous salt has a bright green color. The analyses yielded the following results:

I. 0.2358 gram dried in the air lost 0.0293 gram H_2O at 200° and gave 0.0325 gram CuO.

II. 0.3473 gram dried in the air lost 0.043 gram H_2O at 200° and gave 0.0482 gram CuO.

	Calculated.		Found.	
			I.	II.
$(C_9H_{10}SNO_4)_2$ ...	456.	77.11	...	...
Cu ...	63.4	10.72	11.01	10.79
$4H_2O$ ...	72.	12.17	12.42	12.38
	591.4	100.00		

Jacobsen* states that this salt contains only three molecules of

*Loc. cit.

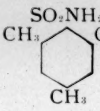
water of crystallization. He has not, however, as yet communicated his analytical data.

The *silver salt* was prepared by adding a solution of silver nitrate to a dilute, neutral solution of the ammonium salt. It was at once thrown down as a heavy white precipitate, which could be dissolved in water only with difficulty. This precipitate was filtered off and washed until no trace of nitric acid could be detected, and, after drying in the air, it was analyzed. Heated up to 160°, its weight remained constant.

I. 0.203 gram salt gave 0.0685 gram Ag.
II. 0.2303 gram salt gave 0.07815 gram Ag.
III. 0.322 gram salt gave 0.1088 gram Ag.

These results correspond respectively to 33.74, 33.93, and 33.78 per cent. silver, or a mean of 33.81 per cent. The formula, $C_6H_2SO_2NH_2(CH_3)_2COOAg$, requires only 32.14 per cent., so that we find an excess of 1.67 per cent. It is difficult to account for this, as every precaution was taken to insure purity of the salt. It is curious that the results found correspond to that required by a salt containing a molecule of water less than silver sulphaminemesitylenate. It is barely possible that the precipitate formed is a compound of the formula $C_6H_2\begin{cases}(CH_3)_2\\SO_2NAg,\\CO\end{cases}$ or the sulphinide in which the hydrogen atom of the imide group is replaced by an atom of silver. This would require 33.96 per cent. silver, a figure which agrees very well with the 33.81 per cent. found. Improbable as this supposition may appear, it is not entirely without analogy, as it is known that the amides of some of the aromatic sulphonic acids furnish silver compounds in which the silver is situated in the ammonia residue.

It is thus shown at least that when mesitylenesulphamide is treated with chromic acid only one of the methyl groups is oxidized, while the other two remain unchanged. The conclusion which would naturally be drawn from this fact, if the results obtained in other similar cases be taken into account, is that the para methyl group is the one that has been changed, the other groups being protected. On the other hand, as it has been shown that the kind of combination characteristic of the sulphinides is found in compounds in which the SO_2NH_2 group and the COOH are in the ortho position with reference to each other, and has not been

observed in other cases, we would be led to believe that mesitylenic sulphinide is derived from orthosulphaminemesitylenic acid, 

According to this it is an ortho methyl group which is oxidized, and not the para group, as was supposed. The question remains, as far as our results are concerned, an open one. In the concluding part of this paper this subject will be discussed more fully, and some other facts bearing upon it will then receive consideration.

Formation of a Bibasic Acid from Mesitylenesulphamide.

When the chromic acid oxidizing mixture from which mesitylenic sulphinide has been separated is allowed to stand for a time, or is concentrated by evaporation on a water-bath, a second product is obtained in small quantity. This was separated from the mixture and purified by crystallization. It crystallizes well from water in the form of large transparent plates, grouped together in bunches. It is more easily soluble in water, alcohol and ether than the sulphinide. It fuses at 279°. It was found to be a strong acid, and some of its salts were prepared and analyzed. Although the results of the analyses do not agree well for any probable formula, the amount of barium found in the barium salt showed clearly that the substance is a bibasic acid. Then, further, the acid was heated in a sealed tube with concentrated hydrochloric acid at 230°, and a product obtained which corresponds very closely to uvitic acid. It is much more difficultly soluble than the original acid, and separates from the solution, on cooling, in the form of fine needles, which fuse well at 288–289°. There can be little doubt that the acid with these properties is uvitic acid, and it follows that the new product is either sulphamineuvitic acid or the corresponding sulphinide.

It is hence evident that, when mesitylenesulphamide is treated with chromic acid, two methyl groups, one of which must be situated in the ortho position with reference to the sulphamide group, are oxidized. But it is an important fact that *only a very small quantity of the bibasic acid is formed.* These results suggest those obtained in connection with the sulphamides of meta- and paraxylene. It will be remembered that *very small quantities* of bibasic acids were also obtained from these compounds.

In order to obtain the bibasic acid in larger quantity, the sulphamide was treated with potassium permanganate in excess. The

acid was readily obtained, and, under the conditions of our first experiments, it was the sole product of the oxidation. If the permanganate solution be added gradually to the solution of the sulphamide the results are different, as Jacobsen* has recently found; and later experiments of our own confirm, in this respect, the results obtained by him. We have also found that, when larger quantities of the sulphamide are subjected to oxidation with the permanganate, there is formed some of the sulphinide, and, on evaporating the filtrate from the manganese hydroxides, there are thrown down on the addition of hydrochloric acid three substances: (1) the bibasic acid fusing at 279°; (2) mesitylenic sulphinide; and (3), if the hydrochloric acid be not too concentrated, the acid potassium salt of the bibasic acid.

The free acid was converted into the barium salt by boiling it with barium carbonate in water. It is easily soluble in water, and could not be prepared in crystallized form. When once separated from the aqueous solution, it dissolves with difficulty. It contains water of crystallization, which it gives up partially in contact with the air. The salt obtained by oxidation with permanganate was analyzed with the following results:

I. 0.3857 gram lost 0.046 gram H_2O at 290°, and gave 0.1999 gram $BaSO_4$.

II. 0.3065 gram lost 0.0369 gram H_2O at 290°, and gave 0.1588 gram $BaSO_4$.

	Calculated.			Found.	
				I.	II.
$C_9H_7SNO_6$	... 257	...	57.37	...	...
Ba	... 137	...	30.58	30.47	30.46
$3H_2O$	... 54	...	12.05	11.93	12.03
	448				

The results agree with those required for the formula $C_6H_2.CH_3.SO_2NH_2.(COO)_2Ba + 3H_2O$, or the acid from which it is derived is sulphamineuvitic acid.

By fusing the acid with potassium hydroxide a new substance was obtained, which has in general the properties of the oxy-acids. It is very difficultly soluble in hot water, and practically insoluble in cold water. It fuses at 294–295°. It separates from a hot aqueous solution in very small compact crystals. It is easily soluble in alcohol and ether, and insoluble in chloroform. Its solution

* Ber. deutsch. chem. Gesell. 12, 604.

is colored red by ferric chloride; the color is, however, not strong, and as we have no good guarantee that our acid was perfectly pure, it may be that this coloration is due to the presence in small quantity of some other oxy-compound.

The *barium salt* of the oxy-acid was obtained in the form of a peculiar looking, gelatinous mass, easily soluble in water.

The *calcium salt* forms delicate, interlacing needles, which have a slight brown color. This salt was analyzed, and the results agree moderately well with those required for the calcium salt of *oxyuvitic acid.*

I. 0.1317 gram salt lost 0.0321 gram H_2O at 200°, and gave 0.0566 gram $CaSO_4$.

II. 0.165 gram salt lost 0.0409 gram H_2O at 200°, and gave 0.0705 gram $CaSO_4$.

	Calculated.			Found.	
				I.	II.
$C_9H_6O_5$	... 194	...	...	...	...
Ca	... 40	...	13.07	12.63	12.56
$4H_2O$	... 72	...	23.53	24.37	24.78
	306		100.00		

The results for the water of crystallization agree very poorly with those required by the formula. Calculating the results for calcium on the basis of the anhydrous salt, the amount required is 17.10 per cent., while the results obtained correspond to 16.71 and 16.70 per cent. respectively.

The sulphamineuvitic acid first obtained was formed by the oxidation of the *sulphamide* with potassium pyrochromate or potassium permanganate. The *sulphinide* was now subjected in turn to the action of each of these oxidizing agents. A marked difference was observed in the two cases. The permanganate readily converts the sulphinide into the bibasic acid, the yield being very good. This method appears, indeed, to be the best one for the preparation of the new acid. On the other hand, pure *mesitylenic sulphinide may be boiled with the usual chromic acid mixture for days without undergoing material change.* In one experiment performed with a weighed quantity of the sulphinide the boiling was continued for four days. Almost the entire quantity taken of the original substance was recovered, and only a trace of the bibasic acid could be detected.

Thus far we have been unable to detect a tribasic acid among the products of oxidation of mesitylenesulphamide or mesitylenic sulphinide. The bibasic acid is readily formed, as has been shown, both from the sulphamide and the sulphinide. Whether the bibasic acid obtained by us under different conditions always represented the same compound or not, is a question which we cannot as yet positively answer. The free acid (or sulphinide) had always very nearly the same fusing point, and presented very nearly the same appearance, but there were slight differences observed between the products obtained at different times, which suggested the possibility at least that these products might be isomeric and not identical.

Formation of a Sulphaminemesitylenic Acid.

In a paper published two years after the first results of this investigation had appeared in print, Jacobsen* describes a new product of the oxidation of mesitylenesulphamide with potassium permanganate. This is a substance of the formula, $C_6H_2\begin{cases}(CH_3)_2\\SO_2NH_2,\\CO_2H\end{cases}$ to which is given the name *parasulphaminemesitylenic acid.* This acid was obtained, together with the isomeric ortho-acid, by oxidizing the sulphamide with permanganate. Jacobsen states that a mixture of the two acids is formed, and says nothing concerning the bibasic acid. We have repeated his experiments, and obtained three products: (1) mesitylenic sulphinide (according to Jacobsen orthosulphomesitylenic acid); (2) parasulphaminemesitylenic acid; and (3) the acid potassium salt of the bibasic acid. The formation of the last product was evidently not noticed by Jacobsen. It is possible, of course, that it may not have been formed in his experiments, but it was certainly always formed in ours. As regards the sulphaminemesitylenic acid, a substance corresponding to the one described by Jacobsen under this name was obtained by us. It crystallizes in needles, and fuses at 270° (uncorr.) and 276° (corr.). It was not fully analyzed, but two sulphur estimations which were made gave results corresponding to the formula of sulphaminemesitylenic acid.

I. 0.2995 gram acid gave 0.3044 gram $BaSO_4$.

II. 0.2222 gram acid gave 0.2214 gram $BaSO_4$.

* Ber. deutsch. chem. Gesell. 12, 604.

The formula $C_6H_2\begin{cases}(CH_3)_2\\SO_2NH_2\\CO_2H\end{cases}$ requires 13.97 per cent. sulphur, while the above results correspond respectively to 13.95 and 13.68 per cent. sulphur.

Structure of the Oxidation Products from Mesitylenesulphamide.

In order to learn more in regard to the nature of mesitylenic sulphinide it was fused with potassium hydroxide in the hope that it would be converted into an oxymesitylenic acid. A considerable quantity of the substance was thus fused and the resulting mass treated in the usual manner. The product is a white crystallized acid possessing all the properties of mesitylenic acid. It is volatile with water vapor. It fuses at 166–167°. It is not colored by ferric chloride. Its solubility corresponds to that of mesitylenic acid. All the solutions were carefully examined for oxymesitylenic acid, but only a slightly bluish tint was produced by ferric chloride, even in the last mother-liquor. It is hence exceedingly doubtful whether even a trace of this acid was formed.

From the pure mesitylenic acid the silver salt was prepared. It was found to contain a molecule of water of crystallization, a fact not stated by Fittig* in his paper on mesitylenic acid.

I. 0.13745 gram of the air-dried salt lost 0.00875 gram H_2O at 100°, and gave 0.054 gram Ag.

II. 0.31945 gram salt lost 0.02125 gram H_2O at 100°, and gave 0.125 gram Ag.

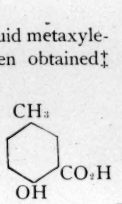
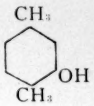
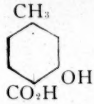
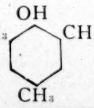
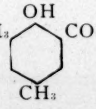
	Calculated.			Found.	
				I.	II.
$C_9H_9O_2$	149	54.19	...	...	...
Ag	108	39.26	...	39.28	39.13
H_2O	18	6.54	...	6.37	6.65
	275	100.00			

The action of fusing potassium hydroxide causes then simply a replacement of the sulphamine group by hydrogen. Some similar cases have previously been observed, among which may be mentioned the formation of salicylic acid by fusing sulphosalicylic acid with potassium hydroxide,† and the formation of oxybenzoic acid from a sulpho-derivative of oxybenzoic acid of unknown composi-

*Annalen der Chemie, 141, 148. †Remsen. Ibid. 179, 107.

tion.* The conditions which cause this apparently abnormal action are not clear.

Jacobsen has recently also made the above observation. He has further shown that, when his parasulphaminemesitylenic acid is fused with potassium hydroxide, it is converted into an oxy-acid isomeric with oxymesitylenic acid. If now we can determine the structure of either of the oxymesitylenic acids, that of the corresponding sulphamine derivatives would be given. In regard to ordinary oxymesitylenic acid one of us (R) has already called attention† to the fact that its structure can be deduced with a fair degree of probability from its mode of formation, by fusion of mesitylenesulphonic acid with potassium hydroxide. The proof is as follows:

By fusing liquid metaxylenol with potassium hydroxide Jacobsen obtained‡ an oxytoluic acid of the formula  , and from paraxylenol  he obtained§ an acid  . Similar results were obtained by fusing thymol and carvacrol—the oxidation took place in the ortho-group. Accordingly, by fusing mesitylenesulphonic acid with alkali, we would expect the formation, first of the oxy-derivative  , and, if the principle indicated in the experiments of Jacobsen is a general one, the formula of oxymesitylenic acid must be  .

The properties of the acid are in harmony with this view. It is volatile with water vapor and gives a color reaction with ferric

* Smith, Journ. pr. Chem. N.F. 16, 231. † Ber. deutsch. chem. Gesell. 11, 2091.
‡ Ibid. 11, 375. § Ibid. 11, 570.

chloride, and the investigations of Tiemann have made it very probable that among the aromatic oxy-acids only those which are derived from salicylic acid possess these two properties. The above formula represents oxymesitylenic acid as a derivative of salicylic acid, whereas, if the acid possessed the other possible structure, it would be a derivative of paraoxybenzoic acid.

After the publication of the above reasoning concerning oxymesitylenic acid, Jacobsen* furnished the experimental proof of the correctness of the view, first expressed by us, by heating the acid with concentrated hydrochloric acid at a high temperature. Under these circumstances carbon dioxide is split off and the corresponding xylenol obtained. The latter was then identified with the 1. 3. 4. xylenol.

Now it would follow, from the fact that parasulphaminemesitylenic acid is converted into an oxymesitylenic acid isomeric with the ordinary variety, that, in the new oxymesitylenic acid, as well as parasulphaminemesitylenic acid, the substituting groups are in the para-position with reference to the carboxyl, and, further, in mesitylenic sulphinide, the residues of the carboxyl and the sulphamine groups are in the ortho-position.

The conclusion to which we are at present forced is, hence, the opposite of that which we anticipated, and, if future experiments should confirm the conclusion, it would appear that, in some cases, there must be other conditions than the position of the substituting group which determine the character of the oxidation. That the position of the groups with reference to each other, or, at least, that something which we at present designate as position, influences very markedly in many cases the character of the oxidation, is clear from many facts known to us, prominent among which may be mentioned those described in the earlier papers of this series. But if position is the only condition governing the process, then, from our previous experiments, it would seem to follow, as a necessary consequence, that when mesitylenesulphamide is oxidized with chromic acid, the two ortho-methyl groups should be protected and the para group oxidized. According to the evidence thus far in our possession, this does not take place.

Before accepting the above evidence as final, it is proposed to repeat on a larger scale some experiments which we have already performed, and which seem to lead to a different conclusion from that above referred to.

* Annalen der Chemie, 195, 279.

In order to determine the structure of mesitylenic sulphinide we went to work in the manner here described: Mesitylenic acid was converted into sulphonic acids. Two were formed, and these can be separated comparatively readily through the barium salts. Both barium salts were converted into the potassium salts. For the present let us call these the α and β salts.

The α salt, treated with phosphorus pentachloride and ammonia, yields an amide which crystallizes in long white needles, and does not fuse at 300°. The same salt, when fused with potassium hydroxide, yields oxymesitylenic acid with all its characteristic properties.

The β salt yields an amide fusing at about 287°; and with potassa an acid fusing at 223°. This latter substance is, in all probability, the parasulphaminemesitylenic acid.

Now, by treating mesitylenic sulphinide with phosphorus pentachloride and ammonia, a substance was obtained which fuses at 287°. According to this, the sulphinide belongs in the same group with the β salt; and, as this salt yields parasulphaminemesitylenic acid, the sulphinide itself would be a para-compound. These last experiments can, however, be regarded only as preliminary, and they are only mentioned now in order to indicate the direction in which the investigation will be continued.

MAY, 1880.

REVIEWS AND REPORTS.

BRIEF REVIEW OF THE MOST IMPORTANT CHANGES IN THE INDUSTRIAL APPLICATIONS OF CHEMISTRY WITHIN THE LAST FEW YEARS.

(Continued from Vol. II, p. 67.)

MATERIALS USED AS FOOD.

Bread.—Probably the most valuable aid has been rendered to bread-making by the careful manufacture on a greatly increased scale of pressed yeast, which improved means of rapid transportation have permitted to be sent in still fresh and sound condition to an ever enlarging circle of consumers. In this country, more than

elsewhere, the use of various "baking powders" prevails, intended to produce carbon dioxide throughout the mass of dough, thus rendering it spongy. Of these preparations two require mention beside the long used cream of tartar and bicarbonate of soda; namely, the acid calcium phosphate (with same alkaline carbonate and a little potassium chloride) of Horsford, now largely and advantageously employed, and the dried ammonium alum with sodium carbonate which has for the last few years been extensively sold, but with very doubtful advantage on the score of wholesomeness.

Meat.—In view of the conditions under which the animals most used for food must be reared, most cheaply at great distances from the dense population by which they will chiefly be consumed, one of the most important of modern industrial problems is that of meat preservation. On the whole, the first place among the many recent attempts at a satisfactory solution may fairly be given to the process of "canning,"—exposure of the meat in suitable vessels, practically cylinders of tin-plate, to a temperature high enough to destroy the vitality of organized ferments, and to expel most of the air from the unoccupied part of the vessel, followed by effectual exclusion of the atmosphere by sealing hermetically with solder. The method may be called recent, since, although fully worked out by Appert as early as 1796–1804, it remained but little used until some fifteen or twenty years ago as compared with its great extension at the present day. It is needless to say that this process is also most useful in its application to fish, milk, vegetables and other forms of perishable food.

Another mode of preserving meat in fit condition for use, excellent in its results, but formerly difficult to carry out in practice, namely, the maintenance of the flesh at a temperature not much above the freezing point, has been brought much more under control by the numerous machines for the production of artificial cold. Although success has attended this plan as applied both for sea and land transportation, the latter commonly with the aid of natural ice, it doubtless admits of being developed upon a larger scale in the future.

Of lately introduced chemical agents to be used as preservatives the most prominent have been salicylic acid and boracic acid or soluble borates. The former, economically manufactured from phenol by Kolbe's synthetic process, is an efficient antiseptic, but limited in its application to meat by its disagreeable taste and the irritant effect it produces upon the fauces when used in needful quantity. The tastelessness of boracic acid, and of the acid phosphates, whose production by its means is, according to Endemann, the chief source of its utility, constitutes an advantage in its favor, but the question of possible danger to health from long continued ingestion of boracic acid or its salts cannot be said to have yet been satisfactorily settled.

Meat Extracts.—Beside the use upon a much larger scale than formerly of meat extract made by Liebig's original process, the in-

troduction is to be noted of analogous products differing therefrom in retaining the animal albumen in uncoagulated form, the evaporation being carried out at temperatures never allowed to reach 60° C. Valentine's "meat juice" represents one of the most carefully prepared of these materials. The process of Leube, published some years ago, involves still another idea, that of bringing into solution the whole of the albumenoids, including the solid muscular fibre, by digestion of the lean meat under pressure with water containing a little hydrochloric acid, neutralizing the free acid with sodium carbonate, and evaporating cautiously to extract consistence. This plan does not seem to have come into general use, nor has any definite reason been given for the failure to employ it.

Preserved Vegetables.—The extensive application of the Appert system of "canning" to fresh vegetable food, tomatoes, peas, young Indian corn, and the like, has been supplemented by the process of desiccation, admirably carried out by Chollet & C^ie^ of Paris, among other firms. The vegetables to be thus preserved are exposed for a short time to the action of steam under considerably more than normal pressure, then rapidly dried in a current of warm air, and finally pressed hard into cakes under a hydraulic press. As an addition to a soldier's ration, these cakes deserve attention from their wholesomeness, the very fair degree in which the fresh odor and flavor are retained for a considerable time, and the convenient form presented for transportation. The now celebrated *Erbswurst* of the Franco-Prussian war involves the principle of desiccation along with that of admixture with fat, but is chiefly noteworthy on the ground of its supplying albumenoid food from a vegetable source and in concentrated and portable form. Desiccation alone has also been usefully applied to eggs, the yolks and whites of which, carefully dried at a low temperature, can long be preserved in fit state for use in cooking.

Butter and Cheese.—The manufacture of these milk products has, notably in some parts of the United States, tended of late years to pass from domestic hands, as a simple farm industry, into those of firms occupied exclusively with dairy operations, the work being carried on in large factories, fitted up with special plant, and supplied with engine power. The minute details of the manufacture, exact attention to temperature, exclusion of ferments, etc., are looked to with much more care in such establishments than they can well be in private hands.

The "artificial butter," "oleo-margarine," or prepared beef fat of Mouriès, has come into use on a very large scale, and, notwithstanding the prejudice aroused against it by its fraudulent sale as actual butter, it must be counted as a not unwholesome, and under some circumstances a valuable addition to the food resources of the world, it being assumed of course that the manufacture itself is honestly carried out with sound material to work upon.

Sugar.—This important manufacture has in its various stages undergone sundry modifications. In some of the regions of pro-

duction, both from the juice of the cane and from that of the beet, there has been an extension of the practice of making a more or less refined product directly from the crude material, but in general the tendency has been rather in the opposite direction, to a distinct separation of the business of making raw sugar by simple means from the juice, and that of refining this raw sugar for the superior purposes of consumption. Even further subdivision of the industry is largely practised; many producers of beet-roots confining themselves to rasping them to pulp and pressing out the juice, to be sold at a stipulated rate to the sugar-makers proper, and sent to them by means of underground pipes, hundreds of miles of which on the Linard system have been laid in Northern France and in Belgium; while, at the other end of the process of manufacture, the working up of molasses and refinery syrups is often found in other hands than those of the first makers of crystallized sugar with whom they have originated.

The success and actual distribution of the sugar industry in different parts of the world, in whatever form conducted, has varied much from time to time, as in the case of Russia, where the extension of production from beet-root has been wonderfully rapid, and in Austria, where the same industry has notably fallen off; everywhere the influence of tariff and internal revenue legislation has had much to do with modifying the effects of natural conditions and of the progress due to improved methods of production.

In obtaining the juice from beet-root the older use of hydraulic presses has been largely susperseded by the more modern cylinder presses, and of late the horizontal direct-acting filter presses have been used with advantage, both as to the amount of juice obtained and its degree of freedom from fine fragments of vegetable fibre.

The diffusion process, by which thin slices of the fresh root are exhausted of sugar by successive portions of water, has become firmly established in many factories, avoiding the use of costly machinery and much engine power, furnishing a purer juice than that obtained by expression, and in consequence of the systematic use of the water in the successive cylinders of the diffusion battery not seriously increasing the consumption of fuel for evaporation. It is much to be desired that the same process should be generally extended to the extraction of juice from the sugar cane; the feasibility of this having been fairly established by experiments on the full working scale with the apparatus of Robert; no other method seems so likely to remedy the enormous loss of juice, fully one-third of the whole, now experienced in the ordinary mill crushing.

For the purpose of rapidly reducing cane juice by evaporation to the condition of a solid mass, capable of being kept without material alteration and shipped to distant points for manufacture into saleable sugar in the hands of the refiner, the simple and effective apparatus known as Fryer's concretor deserves special attention; already considerable quantities of "concrete" made with it have been shipped from West Indian and South American ports with satisfactory results, both to the sugar planter and refiner.

In the clarification of the juice from beet-root the chief recent modification has been the use of largely increased quantities of lime, to be afterwards removed by a current of carbon dioxide gas as usual, the much larger amount of scums and sediment thus produced proving manageable with the aid of the improved filter presses; saving of bone-black in the subsequent filtration may thus be effected.

The kilns for charring and revivifying the bone-black used in the decolorizing filters have been improved in various points of detail as to construction, method of working, and durability. Decolorization by bone-black has come more frequently into use on plantations making white sugar directly from cane juice, as in some districts in Cuba.

The vacuum pan for evaporation of the juice is also more often to be seen as a portion of the equipment of plantation sugar-houses. In boiling down the juice, whether of cane or beet, the practice has become more common of crystallizing much of the sugar in the vacuum pan itself before transference of the mass to the coolers.

In regard to the crystallization and drainage, although the old fashioned loaf sugar is still made, loose crystals drained and washed in the centrifugal machine have assumed much greater importance, and the former practice of crushing or cutting up loaf sugar into fragments of convenient size to be used in tea, coffee, etc., has been reversed, lumps being now moulded by pressure from loose granular sugar in fine crystals.

In recovering an additional amount of crystallizable sugar from the molasses of first drainage the process of most importance is that of dialysis through parchment paper, to recover much saline matter by osmose before a second crystallization, as originally proposed by Dubrunfaut. The liquid from the water cells of the dialyzer is either fermented and distilled to recover such small amount of sugar as it contains, or is simply evaporated to dryness and the saline residue utilized as manure. Less in use than this, but yet practically employed by a good many factories, is the process for separation of sugar from molasses as sugar lime, washing with alcohol.

In the distinct industry of making starch sugar, the consumption of which by brewers, manufacturers of factitious wines, table syrups and caramel, and in the adulteration of the cheaper grades of brown sugar, has assumed very large proportions, less water is used than formerly and very little acid, but the process is conducted in close vessels under pressure sufficient to allow of the temperature rising to as much as 160° C. The product is to be found in the form of a granulated crystalline mass, in solid blocks, and as a thick, highly viscid syrup, the last containing much dextrine.

Wine.—The manufacture of this, as of all other alcoholic beverages, has been placed upon a more rational basis by the valuable researches on fermentation of Pasteur, Liebig, Rees, Brefeld and others.

Chemical materials have been employed to combat the diseases of the grape-vine in Europe due to fungoid and insect attacks. It seems still doubtful whether the former of these two sources of injury is capable of being reached by sulphur itself, or only by the acid products of its oxidation; if the latter be the case there is enormous waste of material in the flowers of sulphur actually in use.

The most distinctly novel step in modern wine-making itself is doubtless Pasteur's process for destroying organized ferments in the bottles or other close vessels used to finally contain the wine, by heating for half an hour or an hour to 60° or 70° C. Valuable as is this process in principle, it requires care in practically carrying it out, and its use has been restricted in France by the liability to injure the delicate *bouquet* of the finer wines in applying this method to their preservation.

Much so-called chemical skill is ill bestowed upon the fraudulent practice of wine fabrication and adulteration, although it is perhaps more difficult in regard to this than to most other industries to draw the line between adulteration and legitimate variations of ordinary practice, as for instance the use of clarifying materials and special forms of tannin, the employment of plaster in the vats, etc.

Beer.—As an addition to wort made from simple malt, glucose and dextrine made from starch by boiling with dilute acid have come into extensive use.

O'Sullivan and Valentine have introduced an analogous material containing maltose instead of glucose, made by the action of dilute sulphuric acid upon ground rice under carefully regulated conditions of time and temperature, the solution obtained being neutralized with chalk, filtered and evaporated in the vacuum pan to a cake consisting of two-thirds maltose and one-third dextrine. Glycerine is also very largely employed as an addition to the wort, serving to sweeten and give consistence to the beer and to moderate in some degree the fermentation.

In boiling the wort hop-extracts have of late to some extent taken the place of actual hops. It is said that these extracts are often made with light petroleum naphtha as the original solvent.

Pasteur has applied his views of fermentation to the proper cooling of the wort by proposing that, immediately after boiling, it be run off into close vessels, and that in these it be kept covered by a stratum of carbon dioxide drawn from the fermenting vats until it has been cooled down to proper temperature, yeast added and fermentation fairly set up. In the rapid cooling of the wort when contact with the air is not cut off, advantage has been taken of the modern ice machines to produce the required reduction of temperature; some of the forms of such machines less adapted to the actual production of ice, as that worked with air alternately compressed and expanded, answering very well for this purpose, with its moderate cooling of very large masses of liquid.

As affording the means of regulating the fermentation, by the

addition of a very small quantity of foreign material without objectionable effect upon the taste of the beverage, salicylic acid has been proposed by Kolbe and to some extent used.

Pasteur's heating process has been found equally effective for the preservation of bottled beer, such as is largely sent to warm climates, as for that of wine.

Distilled Spirits.—The manufacture of spirit from potatoes has undergone great expansion, especially in Central Europe, while the increase of beet-root production has in various countries, particularly in France, led to a corresponding increase in the distillation of alcohol from the residual molasses.

In making potato spirit the practice has been introduced of rapidly steaming the potatoes under increased pressure, then reducing the pressure to the normal point, rapidly cooling and adding malt for the digestion which is to convert the starch into glucose.

The stills in use are continually improved in their minor details, but with no very recent novelty of importance in the principles of their construction.

One of the most interesting modifications of the system of beet-root spirit distillation has been the new method proposed and worked out by Camille Vincent, for utilizing the *vinasse* left behind in the stills. He evaporates this liquor, and submits the residue to destructive distillation in iron vessels (instead of burning off organic matter in the open air). The black porous material found in these vessels is then leached for potash. The condensible portion of the distillate consists of ammoniacal liquor and tar. From the former of these the novel products of tri-methylamine (along with other amine bases) and, from it, methyl chloride are made—this methyl chloride for use in ice machines, in the extraction of perfumes, and in the coal-tar color industry. The tar yields bases of the pyridine series, for which it is not impossible that a use may ere long be found; a single large distillery at Courrières turns out daily, beside other by-products, 100 kilos of methyl alcohol and 1800 kilos of concentrated solution of salts of tri-methylamine.

Vinegar.—Among the results of Pasteur's investigations of organized ferments has been the practice, made use of in France on an industrial scale, of hastening the usual course of acetic fermentation by transplanting or sowing the vinegar *mycoderma*.

In the German, so-called quick method of vinegar making by filtration of the alcoholic fluid through a mass of porous material, usually wood shavings, this mass being traversed at the same time by an ascending current of air, the importance is better recognized now than formerly of carefully regulating not only the temperature but the rate of supply of the liquid to be acidified and the air, since without attention to this notable losses of material may occur, on the one hand by imperfect oxidation and the formation of aldehyde, on the other by more than inevitable evaporation, and by excessive oxidation to carbon dioxide and water.

Artificial Flavoring Essences.—For some years there has been an extensive manufacture of ethers to be used as flavoring materials for confectionary, soda water and other syrups, etc. Those most largely made are the ethyl and amyl formiates, acetates, butyrates and valerianates, but ethyl pelargonate, methyl and ethyl salicylates, and others are also produced.

The most interesting additions of late to the list of such products have been benzoic aldehyde (artificial bitter almond oil), from coal tar toluene, converted by the prolonged action of chlorine into benzylene chloride, to be distilled with an alcoholic solution of an alkaline hydrate; allyl iso-thiocyanate (black mustard oil) from glycerine, distilled with crystallized oxalic acid so as to yield allyl alcohol, and the alkaline thiocyanates so readily obtained as waste products of the treatment of the ammoniacal liquor of gas-works; and artificial vanilline ($C_8H_8O_3$) procured by Tiemann and Haarmann's process from coniferine ($C_{16}H_{22}O_8$), converted into coniferyl alcohol ($C_{10}H_{12}O_3$) with assumption of the elements of water and elimination of glucose, and then oxidized by chromic acid mixture. The high price of the natural vanilla, and its extensive use in connection with chocolate, liqueurs, confectionary, bonbons, etc., gives special importance to the artificial production of its essential constituent.

Artificial Mineral Waters.—These products, occupying a somewhat doubtful position between the ordinary accompaniments of food and therapeutic agents, form the basis of quite an extensive industry, which has grown to its present magnitude within but a few years. With the long used carbonic acid water as a starting point, numerous effervescent waters containing also saline ingredients are made, and omitting the gaseous impregnation, various natural waters, saline, chalybeate, etc., are imitated more or less closely, while of late the artificial modification of the natural contents of certain mineral springs has, with disputed propriety, been added to the directions in which this industry is pushed forward.

J. W. MALLET.

(*To be continued.*)

NOTES.

On the reversal of the direction of rotation caused by ordinary malic acid by a simple change in the concentration.

It is common to regard the power possessed by many substances of turning the plane of polarization either to the right or the left as

something absolute. The substances are either dextro-rotatory or laevo-rotatory. G. H. SCHNEIDER has now shown that, while a concentrated solution of ordinary malic acid is dextro rotatory, the power diminishes with the addition of water until a solution containing 34.24 per cent. of the acid exerts no influence upon polarized light. If now more water be added the solution is laevo-rotatory, a solution containing only 8.4 per cent. acid turning the plane 2.3° to the left. From a formula given in the paper it is calculated that anhydrous malic acid should turn the plane 5.89° to the right.—(*Ber. d. deutsch. chem. Gesell.* 13, 620.)

The Alkaloids.

A. LADENBURG has previously shown that atropine and hyoscyamine yield the same decomposition-products. He has now succeeded in transforming hyoscyamine into atropine by the three following reactions:

(1) Tropine from atropine and hyoscianic acid from daturine were treated with hydrochloric acid on the water-bath.

(2) Hyoscine from hyoscyamine and tropic acid from atropine were treated in the same way.

(3) Hyoscine from hyoscyamine and hyoscianic acid from hyoscyamine were treated in the same way.

In each case atropine was formed.—(*Ber. d. deutsch. chem. Gesell.* 13, 608.)

On the gases retained by occlusion in aluminium and magnesium.

A short time ago M. DUMAS called attention to the power possessed by molten silver of taking up oxygen in considerable quantity when heated to a high temperature, and of retaining the gas, even after solidification, for a very long period, and perhaps indefinitely. He has since found that if aluminium be heated in a porcelain vessel in a vacuum up to the point of fusion of copper or of silver, it gives up a volume of gas about equal to that of the metal. This was found to be nearly pure hydrogen.

Magnesium treated in a similar way also disengages a gas—about one and a half times its own volume. This was found to be essentially hydrogen, though it was accompanied by the oxides of carbon in greater or less quantity.

During the experiments with magnesium, the author observed that stalactites appeared in the upper part of the vessel in which the metal was heated. On examining the vessel more closely, it was found that all the magnesium had been volatilized and deposited in crystalline form. The crystals were very bright and silver white, and can attain the dimensions necessary for measurements.*—(*Comptes rend.* 90, 1027.)

* In a later note (*Comptes rend.* 90, 1101) M. Des Cloizeaux describes the crystals of magnesium and gives their measurements. They are rhombohedra.

The Research Fund in England.

During the past session the following sums have been granted from the Research Fund by the Council of the London Chemical Society on the recommendation of the Research Fund Committee:—

30*l.* to Mr. M. Whitley Williams, for the elaboration of an improved method of Organic Analysis.

25*l.* to Mr. M. M. P. Muir, for the study of the Chemical Habitudes and Physical Constants of Bismuth Compounds.

15*l.* to Mr. J. M. Thomson, for experiments on the action of Isomorphous Bodies in exciting the Crystallization of Supersaturated Solutions.

50*l.* to Dr. Wright, for the continuation of his investigations of certain points in Chemical Dynamics.

25*l.* to Mr. F. D. Brown, for the continuation of his investigations of the theory of Fractional Distillation.

30*l.* to Mr. Bolas, for the preparation and investigation of Alloys and Compounds of Chromium.

20*l.* to Dr. Japp, for the investigation of the action of the Organo-zinc Compounds on Quinones.

100*l.* to Dr. Armstrong, for the determination of certain physical properties, especially the Refractive Indices of Typical Chemical Compounds.

100*l.* to Dr. Wright, for the determination of Chemical Affinity in terms of Electrical Magnitudes.

100*l.* to Mr. F. D. Brown, for the determination of the Vapor Tension of Pure Compounds and Mixtures.

In the Report of the Committee occurs this passage: The Committee desire to point out to the Council, and to the Fellows at large, the desirability of obtaining further additions to the fund, for without such contributions as these the incomes arising from investments would have been quite inadequate to meet the legitimate demands upon the fund. It is to be expected, and indeed we hope, that these demands will increase rather than diminish, and it is therefore especially necessary that efforts should be made to increase the income of the fund.*

* This Research Fund has done much in England to keep alive the spirit of investigation, and no doubt considerable good work has been done in consequence which otherwise would not have been done. This is not the place to discuss the question as to the reason why such good results are reached by such apparently inadequate means. To us it seems perfectly clear. But it may not be out of place to suggest that a Research Fund would find an excellent field in this country.—Ed.

ERRATUM.

In the title of the paper by H. W. Wiley, p. 48, Vol. II, read "chromate" for "sulphate."